OXIDE POLYCRYSTALLINE BASIC MATERIAL AND OXIDE SUPERCONDUCTING CONDUCTOR AND MANUFACTURE THEREOF

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Inventor(s):

IIJIMA YASUHIRO; HOSAKA MARIKO; SADAKATA NOBUYUKI; SAITO TAKASHI; TANABE NOBUO

Applicant(s)::

FUJIKURA LTD

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Abstract

PROBLEM TO BE SOLVED: To speed up the formation of a polycrystalline thin film having good crystalline orientation on a high-strength basic material by constituting an oriented polycrystalline basic material, on which an orient function layer is superimposed and which is also equipped with an orientated polycrystalline intermediate layer, of a metal with high melting point and high hardness of a cubic crystal system having a rolled aggregate structure. SOLUTION: A tape-shaped or otherwise-shaped basic material 1, which has a recrystallized aggregate structure made by heat-treating a non-magnetic alloy, etc., of a cubic system of Hv>=150 of Ni-Cr base, W-Mo base, Fe-Cr base, or Fe-Ni base, or the like at a temperature higher than a recrystallization temperature for hours after hot-rolling of 90% or more, is good in crystalline orientation. An orientated polycrystalline thin film 2 is continuously formed of particles such as yttrium-stabilized zirconia, CaO2 or Y2 O3 deposited on a filming surface on the basic material 1, preferably at the sometime with irradiation of an ion beam from an oblique direction of a normal line to the surface. An oxide superconducting conductor 5, etc., is made up by superimposing an oxide superconducting layer 4 on an upper surface thereof. Because the particles deposited on the basic material 1 deposit, in the initial stage, as atoms with good orientation property, film forming speed is increased.

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(71)出顧人 000005186

株式会社フジクラ

東京都江東区木場1丁目5番1号

(72)発明者 飯島 康裕

東京都江東区木場1丁目5番1号 株式会

社フジクラ内

(72)発明者 保坂 真理子

東京都江東区木場1丁目5番1号 株式会

社フジクラ内

(72)発明者 定方 伸行

東京都江東区木場1丁目5番1号 株式会

社フジクラ内

(74)代理人 弁理士 志賀 正武 (外3名)

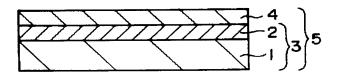
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(54) [発明の名称] 配向性多結晶基材と酸化物超電導導体およびその製造方法

(57)【要約】

【課題】 本発明は、結晶配向性に優れた多結晶薄膜を基材上に従来よりも速い成膜速度で堆積させることができることを目的とするとともに、強度や硬度の高い基材を用いてその上に結晶配向性の高い多結晶薄膜を形成し、配向性に優れた多結晶薄膜を有すると同時に強度の高い基材を備えた酸化物超電導導体を製造する技術の提供を目的とする。

【解決手段】 本発明は、基材1と配向性多結晶中間層2を具備してなり、更に配向性機能層3が積層される配向性多結晶基材3であって、立方晶系の高融点の高硬度金属からなり、圧延集合組織とされたことを特徴とする。



【特許請求の範囲】

【請求項1】 基材と配向性多結晶中間層とを具備してなり、更に配向性機能層が積層される配向性多結晶基材であって、前記基材が立方晶系の高融点の高硬度金属からなり、圧延集合組織とされたことを特徴とする配向性多結晶基材。

【請求項2】 立方晶系の高融点の高硬度金属からなり、圧延集合組織とされた基材と、この基材上に形成された配向性多結晶中間層と、この配向性多結晶中間層上に形成された酸化物超電導層とを具備してなることを特 10 徴とする酸化物超電導導体。

【請求項3】 立方晶系の高融点の高硬度金属からなる素材に対し、加工度90%以上の圧延加工を施した後に再結晶温度以上の温度に加熱する熱処理を施して基材を形成し、この基材上に中間層の構成粒子を堆積させると同時に斜め方向からイオンピームを照射して配向性多結晶中間層を形成するとともに、この配向性多結晶中間層上に酸化物超電導層を積層することを特徴とする酸化物超電導導体の製造方法。

【発明の詳細な説明】

[0001]

【発明の属する技術分野】本発明は、テープ状などの基材上に結晶配向性に優れた中間層を備えたもの、および、更にその上に超電導特性の優秀な酸化物超電導層などの配向性機能層を備えた構造とその製造方法に関する。

[0002]

【従来の技術】近年になって発見された酸化物超電導体は、液体窒素温度を超える臨界温度を示す優れた超電導体であるが、現在、この種の酸化物超電導体を実用的な 30 超電導導体として使用するためには、種々の解決するべき問題点が存在している。その問題点の1つが、酸化物超電導体の臨界電流密度が低いという問題である。

【0003】酸化物超電導体の臨界電流密度が低いという問題は、酸化物超電導体の結晶自体に電気的な異方性が存在することが大きな原因となっており、特に酸化物超電導体はその結晶軸の a 軸方向と b 軸方向には電気を流し易いが、c 軸方向には電気を流しにくいことが知られている。このような観点から酸化物超電導体を基材上に形成してこれを超電導導体として使用するためには、基材上に結晶配向性の良好な状態の酸化物超電導体を形成し、しかも、電気を流そうとする方向に酸化物超電導体の結晶の a 軸あるいは b 軸を配向させ、その他の方向に酸化物超電導体の c 軸を配向させる必要がある。

【0004】ところで、酸化物超電導体を導電体として使用するためには、テープ状などの長尺の基材上に結晶配向性の良好な酸化物超電導層を形成する必要がある。ところが、金属テープなどの基材上に酸化物超電導層を直接形成すると、金属テープ自体が多結晶体でその結晶構造も酸化物超電導体と大きく異なるために、結晶配向 50

性の良好な酸化物超電導層は到底形成できないものであ る。しかも、酸化物超電導層を形成する際に行なう熱処 理によって金属テープと酸化物超電導層との間で拡散反 応が生じるために、酸化物超電導層の結晶構造が崩れ、 超電導特性が劣化する問題がある。そこで本発明者ら は、ハステロイテープなどの金属テープからなる図4に 示すような基材10の上にイットリウム安定化ジルコニ ア (YSZ) などの多結晶薄膜(中間層)11を形成 し、この多結晶薄膜11上に、酸化物超電導体の中でも 臨界温度が約90Kであり、液体窒素(77K)中で用 いることができる安定性に優れたY, B a, C u, O, 系の 超電導層12を形成することで超電導特性の優れた超電 **導導体13を製造する試みを種々行なっている。このよ** うな試みの中から本発明者らは先に、結晶配向性に優れ た多結晶薄膜を形成するために、あるいは、超電導特性 の優れた超電導テープを得るために、特願平3-126 836号、特願平3-126837号、特願平2-20 5551号、特願平4-13443号、特願平4-29 3 4 6 4 号、特願平 5 - 2 1 0 7 7 7 号などにおいて特 20 許出願を行なっている。

【0005】これらの特許出願に記載された技術によれ ば、成膜処理容器内に設けたターゲットの構成粒子をハ ステロイテープなどのテープ状の基材上に堆積させる際 に、イオンソースから発生させたイオンピームを基材の 成膜面の法線に対して斜め方向からある特定の入射角度 (50~60度)で照射しつつ堆積させ、基材上に多結 晶薄膜を形成する方法 (イオンピームアシスト蒸着法: IBAD法)により、結晶配向性に優れた多結晶薄膜を 形成することができる。この多結晶薄膜は、立方晶系の 結晶構造を有する微細な結晶粒が、多数、結晶粒界を介 して接合一体化されてなり、各結晶粒の結晶軸のc軸は 基材の上面(成膜面)に対して直角に配向されており、 各結晶粒の結晶軸のa軸どうしおよびb軸どうしが互い に同一方向に向けられて基材の成膜面と平行な面に沿っ て面内配向されており、また、図6に示すように多結晶 薄膜11を構成する各結晶粒20のa軸(あるいはb 軸)どうしは、それらのなす角度(粒界傾角K)を30 度程度以下に揃えて配向しているものである。そして更 に、この結晶配向性に優れた多結晶薄膜上にYBaCu ○系の超電導層をレーザー蒸着法等により成膜するなら 40 ば、酸化物超電導層の結晶配向性も優れたものになり、 これにより、77Kで臨界電流密度が10°A/cm²以 上と髙い酸化物超電導導体を得ることができる。

【0006】ところで、先に説明した I B A D 法を利用して製造された酸化物超電導導体 13の他に、図5に示すようなN i あるいはA g からなる配向性金属テープを基材 15とし、その上に反応防止中間層 16と酸化物超電導層 17を積層してなる構造の酸化物超電導導体 18が知られている。この種の酸化物超電導導体において

は、NiあるいはAgからなる金属テープに圧延加工を

施してその組織を集合組織として組織的な配向性を高め、この配向性金属テープを基に反応防止中間層と酸化物超電導層の結晶配向性を高めようとした構造である。 【0007】

【発明が解決しようとする課題】本発明者らが開発した IBAD法による酸化物超電導導体13は、優れた臨界 電流密度を示すものとして知られているが、中間層とし て用いる多結晶薄膜11を成膜するために時間がかかり 製造効率が悪いという問題があった。これはIBAD法 が、イオンビームを斜め方向から照射しながらYSZの 10 原子の堆積を行う際に、並びの悪い配向性の悪いエネル ギー的に不安定な原子をイオンピームのスパッタ効果で 弾き飛ばして除去し、並びの良い配向性の良好なエネル ギー的に安定な原子のみを選択的に残して堆積させるこ とで配向性の良好な多結晶薄膜を得ようとする技術であ るので、スパッタによる原子の堆積効率が低下するため に、通常のスパッタによる成膜に比べて成膜レートが悪 いことに起因している。なおここで、本発明者らが原子 の堆積の状態を観察した結果、IBAD法による原子の 堆積の進行は、初期において特に遅く、ある程度の厚さ の配向性の良好な原子が堆積した後では比較的速いこと が判明した。これは、原子の堆積の初期段階においては 特に並びの悪い配向性の悪い状態の原子が堆積しようと するが、これら多くの並びの悪い原子をイオンビームが 弾きとばす結果、堆積の初期段階において特に成膜レー トが悪く、ある程度配向性が整った状態で原子堆積が進 行した後は、その後に堆積される原子は良好な配向性で 堆積する確立が高いためであると思われる。今回本発明 者らは、このようなIBAD法に基づき、結晶配向性に 優れた多結晶薄膜を基材上に従来よりも速い成膜速度で 堆積させることができることを目的として本願発明に到 達した。

【0008】次に、図5に示すような配向性金属テープ の基材15を用いた従来構造の酸化物超電導導体18 は、基材15の圧延による集合組織を利用した構造であ るために、Ni、Agなどの比較的柔らかい基材(Ag は $Hv=20\sim30$ 、NidHv=80程度)を用いる必 要があった。ここで、超電導導体の適用技術は超電導磁 石あるいは超電導発電機などのように強大な磁力や大き な機械力が作用する部材に適用されるので、基材はでき 40 る限り硬度や強度の高いものが好ましいがNiやAgで は強度不足になるおそれがある。また、Niはそれ自身 強磁性を有するために、磁場応用の基材には適用できな い問題がある。本発明者らはこのような従来構造の問題 に鑑み、強度や硬度の高い基材を用いてその上に結晶配 向性の高い多結晶薄膜を形成し、配向性に優れた多結晶 薄膜を有すると同時に強度の高い基材を備えた酸化物超 電導導体を製造する技術の提供を目的とする。

[0009]

【課題を解決するための手段】本発明は前記課題を解決 50

するために、基材と配向性多結晶中間層とを具備してなり、配向性機能層が積層される配向性多結晶基材であって、基材が立方晶系の高融点の高硬度金属からなり、圧延集合組織とされたことを特徴とする。更に本発明は、立方晶系の高融点の高硬度金属からなり、圧延集合組織とされた基材と、この基材上に形成された配向性多結晶中間層と、この配向性多結晶中間層上に形成された酸化物超電導層とを具備してなる。次に本発明は、立方晶系の高融点の高硬度金属からなる素材に対し、加工度90%以上の圧延加工を施した後に再結晶温度以上の温度に加熱する熱処理を施して基材を形成し、この基材上に中間層の構成粒子を堆積させると同時に斜め方向からイオンビームを照射して配向性多結晶中間層を形成するともに、この配向性多結晶中間層上に酸化物超電導層を積層することを特徴とする。

[0010]

【発明の実施の形態】図1は本発明に係る多結晶基材に 酸化物超電導層を積層してなる酸化物超電導導体の一実 施形態の断面構造を示すもので、この実施形態の酸化物 超電導導体1は、テーブ状などの基材1の上面に中間層 (配向性多結晶薄膜) 2が積層されて多結晶基材3が構 成され、この多結晶基材3の上面に酸化物超電導層(配 向性機能層) 4が積層されてテーブ状の酸化物超電導導 体5が構成されている。前記基材1は、Ni-Cr系 (具体的には、Ni-Cr-Fe-Mo系のハステロイ B、C、X等)、W-Mo系、Fe-Cr系(例えば、オ ーステナイト系ステンレス)、Fe-Ni系(例えば、 非磁性の組成系のもの)などの材料に代表される立方晶 系のHv=150以上の非磁性の合金からなることが好 ましく、これらの系の合金に90%以上の熱間圧延加工 が施され、更にその後に再結晶温度(1200~150 0℃) 以上の温度で数時間、例えば、1500℃の温度 で5時間の熱処理が施されて再結晶集合組織とされたも のである。また、基材1の表面は表面粗さ ± 1 0 \sim 20 nm、面内配向性を示すFWHM(半値全幅)の値が1 0°程度とされていることが好ましい。

【0011】前記ハステロイは、 $Cr:1\sim23.0$ %、 $Fe:4\sim20\%$ 、 $Mo:8\sim30\%$ 、 $Co:0.5\sim2.5\%$ 、 $W:0.2\sim4.5\%$ 、残部Niの組成を主体とすることで知られるもので、 $Hv=200\sim400$ の範囲の硬度が高いものである。 これらのハステロイに代表されるNi-Cr系の合金は、いずれも、高硬度の合金であり、90%以上の強加工後に再結晶温度以上で熱処理されることで集合組織とされて良好な結晶配向性を示すようになる。前記中間層(配向性多結晶薄膜) 2は、イットリウム安定化ジルコニア(YS2)、酸化セリウム(CeO_1)、酸化イットリウム(Y_1O_1)などからなり、本発明者らが特許出願している前述のIBAD法により基材 1上に成膜したものである。【0012】図3は、基材 1上に形成される中間層2の

製造に好適に用いられる多結晶薄膜の製造装置の一例を示す図である。この多結晶薄膜の製造装置は、テープ状の基材1を支持するとともに所望温度に加熱することができる基材ホルダ23と、基材ホルダ23上にテープ状の基材1を送り出すための基材送出ボビン24と、多結晶薄膜が形成されたテープ状の基材1を巻き取るための基材巻取ポビン25と、前記基材ホルダ23の斜め上方に所定間隔をもって対向配置された板状のターゲット36の下面に向けて配置されたスパッタビーム照射装10置(スパッタ手段)38と、前記基材ホルダ23の側方に所定間隔をもって対向され、かつ、前記ターゲット36と離間して配置されたイオンソース39とが真空排気可能な成膜処理容器40内に収納された概略構成となっている

【0013】前記基材ホルダ23は、内部に加熱ヒータを備え、基材ホルダ23の上に送り出されたテープ状の基材1を必要に応じて所望の温度に加熱できるようになっている。この基材ホルダ23はピン等により支持体23aに回動自在に取り付けられており、傾斜角度を調整20できるようになっている。このような基材ホルダ23は、成膜処理容器40内のイオンソース39から照射されるイオンビームの最適照射領域に配設されている。

【0014】この例の多結晶薄膜の製造装置においては、前記基材送出ボビン24から基材ホルダ23上にテープ状の基材1を連続的に送り出し、前記最適照射領域で多結晶薄膜が成膜された基材1を基材巻取ボビン25で巻き取ることで基材1上に連続成膜することができるようになっている。この基材巻取ボビン25は、前記最適照射領域の外に配設されている。

【0015】前記ターゲット36は、目的とする多結晶 薄膜を形成するためのものであり、目的の組成の多結晶 薄膜と同一組成あるいは近似組成のものなどを用いる。 ターゲット36として具体的には、MgOあるいはY, O,で安定化したジルコニア (YSZ)、酸化セリウム (CeO,)、酸化イットリウム(Y,O,) などを用い るがこれらに限るものではなく、形成しようとする多結 晶薄膜に見合うターゲットを適宜用いれば良い。このよ うなターゲット36は、ピン等によりターゲット支持体 36aに回動自在に取り付けられており、傾斜角度を調 40 整できるようになっている。前記スパッタビーム照射装 置(スパッタ手段)38は、容器の内部に、蒸発源を収 納し、蒸発源の近傍に引き出し電圧をかけるためのグリ ッドを備えて構成されているものであり、ターゲット3 6に対してイオンビームを照射してターゲット36の構 成粒子を基材22に向けて叩き出すことができるもので ある。

【0016】前記イオンソース39は、スパッタビーム 照射装置38と略同様の構成のものであり、容器の内部 に蒸発源を収納し、蒸発源の近傍に引き出し電圧をかけ 50

るためのグリッドを備えて構成されている。そして、前記蒸発源から発生した原子または分子の一部をイオン化し、そのイオン化した粒子をグリッドで発生させた電界で制御してイオンピームとして照射する装置である。前記イオンソース39は、図3に示すようにその中心軸線 Sを基材ホルダ23上の基材1の成膜面 (表面) に対して入射角度 θ (基材1の垂線(法線) Hと中心線Sとのなす角度)でもって傾斜させて対向されている。この入射角度 θ は50~60度の範囲が好ましいが、より好ましくは55~60度の範囲、最も好ましくは55度前後である。従ってイオンソース39は基材22の成膜面の法線Hに対してある入射角度 θ でもってイオンピームを照射できるように配置されている。

【0017】なお、前記イオンソース39によって基材 22に照射するイオンビームは、YSZの中間層2を形 成する場合はHe'、Ne'、Ar'、Xe'、Kr'など の希ガスのイオンビーム、あるいは、それらと酸素イオ ンの混合イオンビームなどで良いが、СеО,を形成す る場合はX e⁺、K r⁺あるいはこれら2元素の混合イオ ンピームを用いる。また、前記成膜処理容器40には、 この容器40内を真空などの低圧状態にするためのロー タリーポンプ51およびクライオポンプ52と、ガスボ ンべなどの雰囲気ガス供給源がそれぞれ接続されてい て、成膜処理容器40の内部を真空などの低圧状態で、 かつ、アルゴンガスあるいはその他の不活性ガス雰囲気 または酸素を含む不活性ガス雰囲気にすることができる ようになっている。さらに、前記成膜処理容器40に は、この容器40内のイオンピームの電流密度を測定す るための電流密度計測装置55と、前記容器40内の圧 力を測定するための圧力計55が取り付けられている。

【0018】次に前記構成の製造装置を用いてテープ状の基材1上にYSZの多結晶薄膜を形成する場合について説明する。テープ状の基材22上に多結晶薄膜を形成するには、YSZからなるターゲット36を用い、基材22を収納している成膜処理容器40の内部を真空引きして減圧雰囲気とするとともに、基材送出ボビン24から基材ホルダ23に基材1を所定の速度で送り出し、さらにイオンソース39とスパッタビーム照射装置38を作動させる。

【0019】スパッタビーム照射装置38からターゲット36に対してイオンピームを照射するとターゲット36の構成粒子が叩き出されて基材1上に飛来する。そして、基材ホルダ23上に送り出された基材1上にターゲット36から叩き出した構成粒子を堆積させると同時にイオンソース39から、例えば、Arイオンと酸素イオンの混合イオンビームを照射して所望の厚みの多結晶薄膜を成膜し、成膜後のテーブ状の基材1を基材巻取ボビン25に巻き取る。

【0020】ここでイオンビームを照射する際の入射角度 θ は、 $50\sim60$ 度の範囲が好ましく、より好ましく

は55度前後である。ここで θ を90度とすると、多結晶薄膜のc軸は基材22上の成膜面に対して直角に配向するものの、基材22の成膜面上に(111)面が立つので好ましくない。また、 θ を30度とすると、多結晶薄膜はc軸配向すらしなくなる。前記のような好ましい範囲の入射角度でイオンビーム照射するならば多結晶薄膜の結晶の(100)面が立つようになる。このような入射角度でイオンビーム照射を行ないながらスパッタリングを行なうことで、基材1上に形成されるYSZ0多結晶薄膜の結晶軸のa軸どうしおよびb軸どうしは互いに同一方向に向けられて基材1の上面(成膜面)と平行な面に沿って面内配向させることができる。

【0021】ここで、イオンビームの照射を行いながら 通常の無配向の基材上に原子の堆積を行っていると、原子の堆積の初期段階においては並びの良い配向性の良好 な原子と並びの悪い配向性の悪い状態の原子の両方が堆積しようとするが、これら多くの並びの悪い原子をイオンビームが弾きとばす結果、堆積の初期段階において特に成膜レートが悪くなる。しかし、この形態において用いるのは、予め再結晶集合組織として配向性を高めた基 20材1であるで、この基材1の上に堆積しようとするYS Zの原子は、無配向基材上に堆積しようとする場合よりも良好に配向しようとする結果、配向性の良好な安定な位置に存在する原子の割合が高くなり、堆積の初期段階において並びの良い配向性の良好な原子が堆積しやすくなり、成膜レートが向上するので、配向性の良好な中間層としての多結晶薄膜2が早く生成する。

【0022】そして、前述のようにして形成された多結 晶薄膜2上には酸化物超電導層4が積層され、例えば、 前述のようにして粒界傾角が精度良く揃えられた多結晶 薄膜2上にスパッタリングやレーザ蒸着法などの成膜法 により形成するならば、この多結晶薄膜2上に積層され る酸化物超電導層4も多結晶薄膜2の配向性に整合する ようにエピタキシャル成長して結晶化する。よって前記 多結晶薄膜2上に形成された酸化物超電導層4は、結晶 配向性に乱れが殆どなく、この酸化物超電導層4を構成 する結晶粒の1つ1つにおいては、基材1の厚さ方向に 電気を流しにくいc軸が配向し、基材1の長さ方向にa 軸どうしあるいはb軸どうしが配向している。従って、 得られた酸化物超電導層は、結晶粒界における量子的結 40 合性に優れ、結晶粒界における超電導特性の劣化が殆ど ないので、基材1の長さ方向に電気を流し易くなり、M g〇やSrT〇,の単結晶基材上に形成して得られる酸 化物超電導層と同じ程度の十分に高い臨界電流密度が得 られる。

【0023】ところで、図2に示すように、基材1上に 多結晶薄膜2を成膜した後に、IBAD法ではない通常 のスパッタ法(イオンピームアシストを行わないスパッ タ法やバイアススパッタ法)により多結晶薄膜2上に更 に同一材料製の多結晶薄膜6を成膜して2層構造の中間 50

層を形成しても良い。ここで、IBAD法による結晶配向性の良好な多結晶薄膜2の上に多結晶薄膜6を成膜するならば、多結晶薄膜6は多結晶薄膜2に対してエピタキシャル成長して容易に成長するので、多結晶薄膜6の結晶配向性も充分に高いものとすることができる。このようにするならば、成膜速度の遅いIBAD法の欠点を補う形で充分な厚さの中間層(多結晶薄膜2と多結晶薄膜6を合わせた分の層厚のもの)を容易に得ることができ、充分な厚さの多結晶薄膜2、6を備えた多結晶基材3'を得ることができるとともに、その上に酸化物超電導層4を設けることで図2に示す構造の酸化物超電導導体を得ることができる。

[0024]

【実施例】

(実施例1) ハステロイA (Ni58%、Mo20%、 Mn2.0%、Fe20%)からなる厚さ1mmの金属 テープを用い、超硬合金の加圧ロールを用いてこの金属 テープを熱間圧延加工(600 $m{C}$)数パスで厚さ80 $m{\mu}$ mに強圧延加工した。続いてこの金属テープを再結晶温 度以上の1500℃に5時間加熱後に冷却する熱処理を 施し、再結晶集合組織を有する金属テープ基材を得た。 この圧延後の金属テープの表面粗さの平均値は±20 n m以下であった。続いて、図3に示す構成の多結晶薄膜 の製造装置を使用し、この製造装置の成膜処理容器内部 をロータリーポンプおよびクライオポンプで真空引きし て3.0×10⁻¹トールに減圧した。また、ターゲット はYSZ(安定化ジルコニア)製のものを用い、スパッ 夕電圧1000V、スパッタ電流100mA、イオンソ ースから発生させるイオンビームの入射角度を基材の成 膜面の法線に対して55度に設定し、イオンソースのア シスト電圧を300Vに、イオンソースの電流を60m Aに設定して、基材上にターゲットの構成粒子を堆積さ せると同時にイオンビームを照射して厚さ 0.5 μmの 膜状のYSZの多結晶薄膜を1時間かけて成膜した。

【0025】得られたYSZの多結晶薄膜について、 $CuK\alpha$ 線を用いた $\theta-2\theta$ 法によるX線回折試験を行った結果、YSZの(200)面あるいは(400)面のピークが認められ、YSZの多結晶薄膜の(100)面が基材表面と平行な面に沿って配向しているものと推定することができ、YSZの多結晶薄膜がそのc軸を基材の成膜面に垂直に配向させて形成されていることが判明した。

【0026】次に、このYSZの多結晶薄膜においてYSZの多結晶薄膜のa軸あるいはb軸が配向しているか否かを測定した。その測定のためには、図6に示すように、基材1上に形成された多結晶薄膜2にX線を角度 θ 1で照射するとともに、入射X線を含む鉛直面において、入射X線に対して2010角度の位置にX線カウンター58を設置し、入射X線を含む鉛直面に対する水平角度 ϕ 0値を適宜変更して、即ち、基材1を図6におい

40

10

て矢印に示すように回転角のだけ回転させることにより得られる回折強さを測定することにより多結晶薄膜 2 の a 軸どうしまたは b 軸どうしの配向性を計測した。その結果、この例の多結晶薄膜の場合、 ϕ を 9 0 度と 0 度とした場合、即ち、回転角のに対して 9 0 度おきに Y S Z の (111) 面のピークが現われた。これは、基板面内における Y S Z Z の多結晶薄膜の a 軸どうしまたは b 軸どうしが配向していることが明らかになった。

【0027】さらに、得られたYSZの多結晶薄膜の多結晶層の各結晶粒における結晶配向性を測定した。この測定では図6を基に先に説明した方法でX線回折を行なう場合に、中の角度を-10度~+10度まで1度刻みの値に設定した際の回折ピークを測定した。その結果から、得られたYSZの多結晶薄膜の回折ピークは、粒界傾角±3~5度以内では表われるが、±8~10度では消失していることが判明した。従って、得られた多結晶薄膜の結晶粒の粒界傾角は、10度以内に収まっていることが判明し、良好な配向性を有することが明らかになった。

【0028】次に、前記YSZの多結晶薄膜上にレーザ蒸着装置を用いて厚さ1.0 μ mの酸化物超電導層を形成し、酸化物超電導導体を作製した。このレーザ蒸着装置に備えるターゲットとしては、Y_{1.0}Ba_{2.0}Cu_{3.0}O₇₋₁なる組成の酸化物超電導体からなるターゲットを用いた。成膜処理室の内部を 1×10^{-1} トールに減圧した後、内部に酸素を導入し 2×10^{-1} トールとした後、レーザ蒸着を行なった。ターゲット蒸発用のレーザとして波長193nmのArFレーザを用いた。この成膜後、400°Cで60分間、酸素雰囲気中において薄膜30を熱処理し、酸化物超電導導体を得た。

【0029】この酸化物超電導導体を液体窒素で77Kに冷却し、外部磁場0T(テスラ)の条件で4端子法にて臨界電流密度の測定を行なった結果、臨界電流密度=8.2×10A/cm²を示し、極めて優秀な超電導特性を発揮することが確認できた。

【0030】(比較例)前記実施例の集合組織を有する配向性金属テープの代わりに、加工を施していない無配向のハステロイ製金属テープを用いて実施例と全く同じ処理を施し、基材テープ上に厚さ 0.5μ mの中間層を成膜すのために前記と同じ条件で5時間を要した。この酸化物超電導導体を液体窒素で77K冷却し、外部磁場0T(テスラ)の条件で4端子法で臨界電流密度の測定を行なった結果、臨界電流密度= 8.0×10 A/cm¹を示し、先の実施例と同等の優秀な超電導特性を発揮することを確認できたが、無配向金属テープを用いると中間層の成膜に5倍の時間を要することが明らかになった。

[0031]

【発明の効果】以上説明したように請求項1記載の配向 50

性多結晶基材にあっては、基材と配向性多結晶中間層と を具備してなり、配向性機能層が積層される配向性多結 晶基材であって、立方晶系の高融点の高硬度金属からな り、圧延集合組織とされたものであるので、圧延集合組 織とされた配向性の良好な基材上に容易に配向性の良好 な多結晶中間層を有するものが得られる。そして、配向 性多結晶中間層上に形成する配向性機能層の結晶配向性 も配向性多結晶中間層に合わせて容易に配向させること ができるので、結果的に結晶配向性に優れた配向性機能 層を得ることができる。また、基材は立方晶系の高融点 の高硬度金属からなるので、強度が高く、機械的な応力 が作用しやすい用途に対しても適用できる。

【0032】また、請求項2に記載の超電導導体にあっては、立方晶系の高融点の高硬度金属からなり、圧延集合組織とされた基材と、この基材上に形成された配向性多結晶中間層と、この配向性多結晶中間層上に形成された配向性多結晶中間層とを具備してなることを特徴とするので、圧延集合組織とされた配向性の良好な基材上に容易に配向性の良好な多結晶中間層を有するものが得られるともに、配向性多結晶中間層上に形成する酸化物超電導層の結晶配向性も配向性多結晶中間層に合わせて容易に配向させることができ、結果的に結晶配向性に優れ、超電導特性の優れた酸化物超電導層を得ることができる。また、基材は立方晶系の高融点の高硬度金属からなる。また、基材は立方晶系の高融点の高硬度金属からなるので、強度が高く、機械的な応力が作用しやすい超電導磁石、超電導発電器等の磁場応用用途に対しても強度的な問題なく適用することができる。

【0033】次に、請求項3に記載の発明では、立方晶 系の高融点の高硬度金属からなる素材に対し、加工度 9 0%以上の圧延加工を再結晶温度以上の温度で施して基 材を形成することで再結晶集合組織とすることができ、 結晶配向性の良好な基材とすることができる。そして、 この基材上に中間層の構成粒子を堆積させると同時に斜 め方向からイオンピームを照射して配向性多結晶中間層 を形成することで、配向性多結晶薄膜を構成するべき原 子を基材上に堆積させて並びの悪い不安定な位置にある 原子をイオンビームで除去しながら並びの良い結晶配向 性の良好な原子のみを選択的に残して堆積させる際に、 堆積の初期段階で配向性基材の配向性に合わせて原子を 並びの良い配向性の良い状態に優先的に堆積させること ができるので、基材の配向性に沿うように配向性の良好 な配向性多結晶中間層を従来よりも短い時間で成膜する ことができる。また、配向性多結晶中間層上に酸化物超 電導層を成膜するならば、配向性多結晶中間層上に良好 な結晶配向性でもって酸化物超電導層を成膜できるの で、結果的に臨界電流特性の優れた超電導特性の優れた 酸化物超電導導体を従来方法よりも短い時間で製造する ことができ、製造効率を向上できる効果がある。

【図面の簡単な説明】

【図1】 本発明に係る多結晶薄膜を備えた酸化物超電

11

導導体の第1の実施形態を示す断面図である。

【図2】 本発明に係る多結晶薄膜を備えた酸化物超電 導導体の第2の実施形態を示す断面図である。

【図3】 本発明の多結晶薄膜を製造する際に用いられる多結晶薄膜の製造装置の一例を示す概略構成図である。

【図4】 従来の多結晶薄膜の製造方法を実施して得られた多結晶薄膜の一例を示す断面図である。

【図5】 従来の多結晶薄膜の製造方法を実施して得ら

れた多結晶薄膜の他の例を示す断面図である。

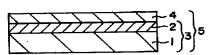
【図6】 多結晶薄膜の結晶配向性を測定するための装置の概念図である。

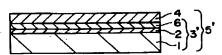
【図7】 多結晶薄膜を構成する結晶粒の結晶配向性を示す略図である。

【符号の説明】

1 ···基材、2 ···配向性多結晶薄膜(配向性多結晶中間層)、3、3 ····多結晶基材、4 ···酸化物超電導層(配向性機能層)、5、5 ····酸化物超電導導体。

【図1】



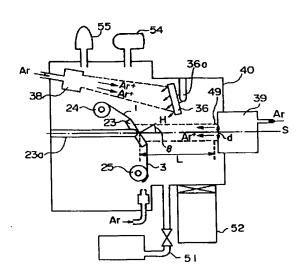


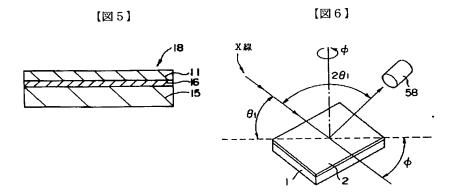
[図2]



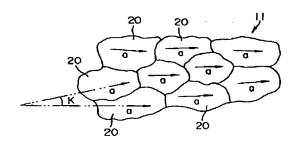
[図4]

[図3]





【図7】



フロントページの続き

(72)発明者 斉藤 隆

東京都江東区木場1丁目5番1号 株式会 社フジクラ内 (72)発明者 田辺 信夫

東京都江東区木場1丁目5番1号 株式会社フジクラ内

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01.08.1997 (72) Inventor: IIJIMA YASUHIRO

HOSAKA MARIKO

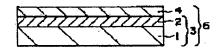
SADAKATA NOBUYUKI

SAITO TAKASHI TANABE NOBUO

(54) OXIDE POLYCRYSTALLINE BASIC MATERIAL AND OXIDE SUPERCONDUCTING CONDUCTOR AND MANUFACTURE THEREOF

(57) Abstract:

PROBLEM TO BE SOLVED: To speed up the formation of a polycrystalline thin film having good crystalline orientation on a high-strength basic material by constituting an oriented polycrystalline basic material, on which an orient function layer is superimposed and which is also equipped with an orientated polycrystalline intermediate layer, of a metal with high melting point and high hardness of a cubic crystal system having a rolled aggregate structure. SOLUTION: A tape-shaped or otherwiseshaped basic material 1, which has a recrystallized aggregate structure made



by heat-treating a non-magnetic alloy, etc., of a cubic system of Hv·150 of Ni-Cr base, W-Mo base, Fe-Cr base, or Fe-Ni base, or the like at a temperature higher than a recrystallization temperature for hours after hot-rolling of 90% or more, is good in crystalline orientation. An orientated polycrystalline thin film 2 is continuously formed of particles such as yttrium-stabilized zirconia, CaO2 or Y2O3 deposited on a filming surface on the basic material 1, preferably at the sometime with irradiation of an ion beam from an oblique direction of a normal line to the surface. An oxide superconductng conductor 5, etc., is made up by superimposing an oxide superconducting layer 4 on an upper surface thereof. Because the particles deposited on the basic

material 1 deposit, in the initial stage, as atoms with good orientation property, film forming speed is increased.

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CLAIMS

[Claim(s)]

[Claim 1] The stacking-tendency polycrystal base material which is a stackingtendency polycrystal base material to which it comes to provide a base material and a stacking-tendency polycrystal interlayer, and the laminating of the stacking-tendency stratum functionale is carried out further, and is characterized by for the aforementioned base material consisting of a high degree-of-hardness metal of the high-melting point of cubic system, and making it into a rolling texture. [Claim 2] the oxide superconductivity characterized by coming to provide the base material which consists of a high degree-of-hardness metal of the high-melting point of cubic system, and was made into the rolling texture, the stacking-tendency polycrystal interlayer formed on this base material, and the oxide-superconductivity layer formed on this stacking-tendency polycrystal interlayer -- a conductor [Claim 3] the oxide superconductivity characterized by carrying out the laminating of the oxide-superconductivity layer on this stacking-tendency polycrystal interlayer while heat treatment heated to the temperature more than a recrystallizing temperature is performed, a base material is formed, an ion beam is irradiated from across and a stacking-tendency polycrystal interlayer is formed at the same time it makes an interlayer's constituent particle deposit on this base material after performing strip processing of 90% or more of workabilities to the material which consists of a high degree-of-hardness metal of the high-melting point of cubic system -- the manufacture technique of a conductor

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[The technical field to which invention belongs] this invention relates to the thing equipped with the interlayer excellent in the crystal stacking tendency on base materials, such as the shape of a tape, and the structure further equipped with tendency stratum functionale, such as an oxide-superconductivity layer with an excellent superconductivity property, on it, and its manufacture technique. [0002]

[Description of the Prior Art] although the oxides superconductors become and discovered at recent years is an outstanding superconductor which shows the critical temperature exceeding liquid nitrogen temperature -- present and this kind of oxides superconductors -- a practical superconductivity -- in order to use it as a conductor, the trouble which should solve various exists One of the trouble of the is the problem that the critical current density of an oxides superconductors is low.

[0003] The problem that the critical current density of an oxides superconductors is low is the cause with big an electric anisotropy existing in the crystal of an oxides superconductors itself, and although especially an oxides superconductors tends to pass the electrical and electric equipment to a shaft orientations and b shaft orientations of the crystallographic axis, it is known that it will be hard to pass the electrical and electric equipment to c shaft orientations, such a viewpoint to an oxides superconductors -- a base-material top -- forming -- this -- a superconductivity -- in order to use it as a conductor, it is necessary to form the oxides superconductors of the good status of a crystal stacking tendency on a base material, to make the orientation of the a-axis or b shaft of the crystal of an oxides superconductors carry out in the orientation which is going to pass the electrical and electric equipment moreover, and to make the orientation of the c axis of an oxides superconductors carry out in the orientation of other

[0004] By the way, in order to use an oxides superconductors as a conductor, it is necessary to form the good oxide-superconductivity layer of a crystal stacking tendency on the base material of long pictures, such as the shape of a tape. However, as for the metal tape itself, if an oxide-superconductivity layer is directly formed on base materials, such as a metal tape, since it differs from an oxides superconductors greatly, the crystal structure cannot form the good oxide-superconductivity layer of a crystal stacking tendency at all by the polycrystalline substance, either. And in order

that a diffusion reaction may arise between a metal tape and an oxidesuperconductivity layer with heat treatment performed in case an oxidesuperconductivity layer is formed, the crystal structure of an oxide-superconductivity layer collapses and there is a problem on which a superconductivity property deteriorates. Then, this invention persons form the polycrystal thin films (interlayer) 11, such as an yttrium stabilized zirconia (YSZ), on the base material 10 which is shown in the drawing 4 which consists of metal tapes, such as a Hastelloy tape. On this polycrystal thin film 11, critical temperature is about 90 K also of an oxides superconductors. the superconductivity which excelled [form / the superconductivity layer 12 of the Y1Ba2Cu3Ox system excellent in the stability which can be used in liquid nitrogen (77K)] in the superconductivity property -- various attempts which manufacture a conductor 13 are performed Out of such an attempt, previously, this invention persons are performing the patent application to Japanese Patent Application No. 126836 [three to], Japanese Patent Application No. 126837 [three to], Japanese Patent Application No. 205551 [two to], Japanese Patent Application No. 13443 [four to], Japanese Patent Application No. 293464 [four to], Japanese Patent Application No. 210777 [five to], etc., in order to form the polycrystal thin film excellent in the crystal stacking tendency, or in order to obtain the superconductivity tape which was excellent in the superconductivity property. [0005] In case the constituent particle of the target prepared in the membrane formation processing container is made to deposit on the base material of the shape of a tape, such as a Hastelloy tape, according to the technique indicated by these patent applications It is made to deposit, irradiating the ion beam generated from the ion source from across to the normal of the membrane formation side of a base material with a certain specific degree (50 - 60 degrees) of incident angle. By the technique (the ion beam assistant vacuum-deposition: IBAD method) of forming a polycrystal thin film on a base material, the polycrystal thin film excellent in the crystal stacking tendency can be formed. The detailed crystal grain which has the crystal structure of cubic system this polycrystal thin film in large numbers Come to carry out junction unification through the grain boundary, and orientation of the c axis of the crystallographic axis of each crystal grain is carried out right-angled to the top (membrane formation side) of a base material. The a-axes and b shafts of a crystallographic axis of each crystal grain are mutually turned in the same orientation, and orientation within a field is carried out along the membrane formation side of a base material, and the parallel field. Moreover, the a-axes (or b shaft) of each crystal grain 20 which constitutes the polycrystal thin film 11 as shown in drawing 6 are arranging and carrying out orientation of those angles (grain-boundary inclination K) to make to about 30 or less degrees. and the thing which forms the superconductivity layer of YBaCuO system by the laser vacuum deposition etc. on the polycrystal thin film excellent in this crystal stacking tendency further and which was excellent also in the crystal stacking tendency of an oxide-superconductivity layer when becoming -becoming -- thereby -- 77K -- the oxide superconductivity with a as high critical current density as two or more 105A/cm -- a conductor can be obtained [0006] by the way, the oxide superconductivity manufactured using the IBAD method explained previously -- the oxide superconductivity of the structure which makes the stacking-tendency metal tape which consists of nickel or Ag which is shown in the drawing 5 other than a conductor 13 a base material 15, and comes to carry out the

laminating of the reaction prevention interlayer 16 and the oxide-superconductivity layer 17 on it -- the conductor 18 is known this kind of oxide superconductivity -- in a conductor, it is the structure which was going to perform strip processing to the metal tape which consists of nickel or Ag, was going to raise the stacking tendency systematic as a texture for the organization to it, and was going to raise the crystal stacking tendency of a reaction prevention interlayer and an oxide-superconductivity layer to it on the basis of this stacking-tendency metal tape

[0007]

[Problem(s) to be Solved by the Invention] the oxide superconductivity by the IBAD method which this invention persons developed -- although known as what shows the outstanding critical current density, in order that a conductor 13 might form the polycrystal thin film 11 used as an interlayer, it required time and had the problem that manufacture luminous efficacy was bad In case the IBAD method deposits the atom of YSZ, irradiating an ion beam from across, this By the spatter effect of an ion beam, flip off the bad atom of the bad stacking tendency of a list unstable in energy, and it is removed. Since it is the technique in which it obtains the good polycrystal thin film of a stacking tendency by leaving alternatively only the good atom of the good stacking tendency of a list stable in energy, and making it deposit In order for the deposition luminous efficacy of the atom by the spatter to fall, compared with membrane formation by the usual spatter, the membrane formation rate originates in the bad thing. In addition, as a result of this invention persons' observing the status of atomic deposition here, especially advance of deposition of the atom by the IBAD method was slow in the first stage, and after the good atom of the stacking tendency of a certain amount of thickness accumulated, the comparatively quick thing made it clear. Although the atom of the bad status of the bad stacking tendency of especially a list tends to deposit this in the initial stage of atomic deposition, as a result of an ion beam's flipping off the bad atom of the list [many] of these, especially in the initial stage of deposition, a membrane formation rate is bad, and after the stacking tendency has been ready to some extent and atomic deposition advances, it is thought that the atom deposited after that is because the establishment deposited by the good stacking tendency is high. This invention persons reached the invention in this application this time based on such an IBAD method for the purpose of the ability to make the polycrystal thin film excellent in the crystal stacking tendency deposit at a membrane formation speed quicker than the former on a base material.

[0008] next, the former using the base material 15 of a stacking-tendency metal tape which is shown in drawing 5 -- the oxide superconductivity of structure -- since a conductor 18 was the structure using the texture by rolling of a base material 15, comparatively soft base materials (Ag is Hv=20-30 and nickel is about [Hv=80]), such as nickel and Ag, needed to be used for it here -- a superconductivity -- since the application technique of a conductor is applied to the member on which mighty magnetism and big mechanical power act like a super-conductive magnet or a superconductivity generator, although what has a degree of hardness high as much as possible and an intensity high as much as possible is desirable as for a base material, it has a possibility of becoming the shortage of an intensity, by nickel or Ag Moreover, since nickel has ferromagnetism in itself, there is an inapplicable problem in the base material of a magnetic field application. the oxide superconductivity equipped with base material with a high intensity while this invention persons had the polycrystal

thin film which formed the high polycrystal thin film of a crystal stacking tendency on it in view of the problem of structure such conventionally using the base material with high intensity and degree of hardness, and was excellent in the stacking tendency -- it aims at technical offer which manufactures a conductor [0009]

[Means for Solving the Problem] It is characterized by being the stacking-tendency polycrystal base material to which it comes to provide a base material and a stackingtendency polycrystal interlayer, and the laminating of the stacking-tendency stratum functionale is carried out, and for a base material consisting of a high degree-ofhardness metal of the high-melting point of cubic system, and making this invention into a rolling texture, in order to solve the aforementioned technical probrem. Furthermore, this invention consists of a high degree-of-hardness metal of the highmelting point of cubic system, and it comes to provide the base material made into the rolling texture, the stacking-tendency polycrystal interlayer formed on this base material, and the oxide-superconductivity layer formed on this stacking-tendency polycrystal interlayer. Next, it is characterized by carrying out the laminating of the oxide-superconductivity layer on this stacking-tendency polycrystal interlayer while this invention performs heat treatment heated to the temperature more than a recrystallizing temperature, forms a base material, irradiates an ion beam from across and forms a stacking-tendency polycrystal interlayer at the same time it makes an interlayer's constituent particle deposit on this base material after performing strip processing of 90% or more of workabilities to the material which consists of a high degree-of-hardness metal of the high-melting point of cubic system.

[Embodiments of the Invention] the oxide superconductivity to which drawing 1 comes to carry out the laminating of the oxide-superconductivity layer to the polycrystal base material concerning this invention -- what shows the cross-section structure of the 1 operation gestalt of a conductor -- it is -- the oxide superconductivity of this operation gestalt -- the laminating of the interlayer (stacking-tendency polycrystal thin film) 2 is carried out to the top of the base materials 1, such as the shape of a tape, the polycrystal base material 3 is constituted and the oxidesuperconductivity layer (stacking-tendency stratum functionale) 4 carries out the laminating of the conductor 1 to the top the aforementioned base material 1 -- a nickel-Cr system (concrete -- Hastelloy B of a nickel-Cr-Fe-Mo system --) W-Mo systems, such as C and X, a Fe-Cr system (for example, austenite stainless steel), It is desirable to consist of a nonmagnetic alloy beyond Hv=150 of the cubic system represented by materials, such as a Fe-nickel system (for example, thing of a nonmagnetic composition system). 90% or more of a hot rolling manipulation is given to the alloy of these systems, heat treatment of 5 hours is performed at the temperature of several hours (for example, 1500 degrees C) further after that with the temperature more than a recrystallizing temperature (1200-1500 degrees C), and it considers as a recrystallization texture. Moreover, as for the front face of a base material 1, it is desirable that the value of FWHM (full width at half maximum) which shows **10-20nm of surface roughnesss and the stacking tendency within a field is made into about 10 degrees.

[0011] It is known for the aforementioned Hastelloy making composition of remainder nickel a subject Cr:1-23.0%, Fe:4-20%, Mo:8-30%, Co:0.5-2.5%, and W:0.2 to 4.5%,

and the degree of hardness of the domain of Hv=200-400 is high. Each alloy of the nickel-Cr system represented by these Hastelloies is an alloy of a high degree of hardness, and it comes to show a good crystal stacking tendency, being used as a texture by being heat-treated after 90% or more of a strong manipulation above a recrystallizing temperature. The aforementioned interlayer (stacking-tendency polycrystal thin film) 2 consists of an yttrium stabilized zirconia (YSZ), a cerium oxide (CeO2), a yttrium oxide (Y2O3), etc., and forms membranes on a base material 1 by the above-mentioned IBAD method in which this invention persons are doing the patent application.

[0012] Drawing 3 is drawing showing an example of the manufacturing installation of the polycrystal thin film used suitable for the manufacture of an interlayer 2 formed on a base material 1. The base-material electrode holder 23 which can be heated to request temperature while the manufacturing installation of this polycrystal thin film supports the tape-like base material 1. The base-material sending-out bobbin 24 for delivering the tape-like base material 1 on the base-material electrode holder 23. The base-material winding bobbin 25 for rolling round the tape-like base material 1 in which the polycrystal thin film was formed. The tabular target 36 by which opposite arrangement was carried out with the predetermined spacing in the slanting upper part of the aforementioned base-material electrode holder 23. The spatter beam irradiation equipment 38 arranged towards the inferior surface of tongue of a target 36 in the slanting upper part of this target 36 (spatter means), The side of the aforementioned base-material electrode holder 23 is countered with a predetermined spacing, and the ion source 39 which estranges with the aforementioned target 36 and has been arranged serves as the outline configuration contained in the membrane formation processing container 40 in which evacuation is possible.

[0013] The aforementioned base-material electrode holder 23 equips the interior with a heating heater, and can heat now the base material 1 of the shape of a tape delivered on the base-material electrode holder 23 to desired temperature if needed. This base-material electrode holder 23 is attached in base material 23a free [rotation] by the pin. etc., and can adjust the degree of tilt angle now. Such a base-material electrode holder 23 is arranged in the optimum irradiation field of the ion beam irradiated from the ion source 39 in the membrane formation processing container 40.

[0014] In the manufacturing installation of the polycrystal thin film of this example, the tape-like base material 1 can be continuously delivered on the base-material electrode holder 23 from the aforementioned base-material sending-out bobbin 24, and continuity membrane formation of the base material 1 by which the polycrystal thin film was formed in the aforementioned optimum irradiation field can be carried out now on a base material 1 by rolling round with the base-material winding bobbin 25. This base-material winding bobbin 25 is arranged out of the aforementioned optimum irradiation field.

[0015] The aforementioned target 36 is for forming the polycrystal thin film made into the purpose, and the thing of the same composition as the polycrystal thin film of the target composition or approximation composition etc. is used for it. What is necessary is not to restrict to these, although the zirconia (YSZ) specifically stabilized by MgO or Y2O3, a cerium oxide (CeO2), a yttrium oxide (Y2O3), etc. are used as a target 36, and just to use suitably the target corresponding to the polycrystal thin film which it is going to form. Such a target 36 is attached in target base material 36a free [rotation]

by the pin etc., and can adjust the degree of tilt angle now. The aforementioned spatter beam irradiation equipment (spatter means) 38 is equipped with the grid for an evaporation source to the interior of a container, pulling out inside near the evaporation source, and applying a voltage to it, is constituted, irradiates an ion beam to a target 36, turns the constituent particle of a target 36 to a base material 22, and start striking it.

[0016] It is the spatter beam irradiation equipment 38 and the thing of the same configuration as abbreviation, and the aforementioned ion source 39 contains an evaporation source inside a container, it is equipped with the grid for pulling out near the evaporation source and applying a voltage, and is constituted. And it is the equipment which a part of atom generated from the aforementioned evaporation source or molecule is ionized, and the ionized grain is controlled by the electric field generated by the grid, and is irradiated as an ion beam. As shown in drawing 3, the aforementioned ion source 39 has the medial-axis line S, makes it incline to the membrane formation side (front face) of the base material 1 on the base-material electrode holder 23 by degree [of incident angle] theta (angle of perpendicular (normal) H of a base material 1, and center line S to make), and has countered. although this degree [of incident angle] theta has the desirable domain of 50 - 60 degrees -- more -- desirable -- the domain of 55 - 60 degrees -- it is over or below 55 degrees most preferably Therefore, the ion source 39 is arranged so that it may have by degree [of incident angle] theta which has received normal H of the membrane formation side of a base material 22 and an ion beam can be irradiated. [0017] In addition, although the ion beam of rare gas, such as helium+, Ne+, Ar+, Xe+, and Kr+, or the mixed ion beam of they and oxygen ion is sufficient as the ion beam which irradiates a base material 22 with the aforementioned ion source 39 when forming the interlayer 2 of YSZ, when forming CeO2, the mixed ion beam of Xe+, Kr+, or these 2 element is used for it. Moreover, controlled-atmosphere sources of supply, such as a chemical cylinder, are connected with the rotary pump 51 for changing the inside of this container 40 into low voltage status, such as a vacuum, and the cryopump 52 at the aforementioned membrane formation processing container 40, respectively, and it can be made the inert gas ambient atmosphere which is in low voltage status, such as a vacuum, about the interior of the membrane formation processing container 40, and contains the inert gas ambient atmosphere or oxygen of argon gas or others now. Furthermore, the current density metering device 55 for measuring the current density of the ion beam in this container 40 and the pressure gage 55 for measuring the pressure in the aforementioned container 40 are attached in the aforementioned membrane formation processing container 40. [0018] Next, the case where the polycrystal thin film of YSZ is formed on the tapelike base material 1 using the manufacturing installation of the aforementioned configuration is explained. In order to form a polycrystal thin film on the tape-like base material 22, while vacuum length of the interior of the membrane formation processing container 40 which has contained the base material 22 is carried out using the target 36 which consists of YSZ and it considers as the reduced pressure ambient atmosphere, a base material 1 is delivered to the base-material electrode holder 23 at the rate of predetermined from the base-material sending-out bobbin 24, and the ion source 39 and the spatter beam irradiation equipment 38 are operated further. [0019] If an ion beam is irradiated from the spatter beam irradiation equipment 38 to a target 36, the constituent particle of a target 36 will start being struck and it will come flying on a base material 1. And from the ion source 39, for example, the mixed ion beam of Ar ion and oxygen ion is irradiated, the polycrystal thin film of desired thickness is formed, and the base material 1 of the shape of a tape after membrane formation is rolled round in the base-material winding bobbin 25 at the same time it makes the constituent particle which it started striking from a target 36 deposit on the base material 1 delivered on the base-material electrode holder 23.

[0020] Degree [of incident angle] theta at the time of irradiating an ion beam here has the desirable domain of 50 - 60 degrees, and it is over or below 55 degrees more preferably. If theta is made into 90 degrees here, although orientation of the c axis of a polycrystal thin film is carried out right-angled to the membrane formation side on a base material 22, since a field (111) stands on the membrane formation side of a base material 22, it is not desirable. Moreover, if theta is made into 30 degrees, a polycrystal thin film will stop carrying out even c axis orientation. If ion beam irradiation is carried out with the degree of incident angle of the above desirable domains, the field (100) of the crystal of a polycrystal thin film will come to stand. Performing ion beam irradiation with such a degree of incident angle, by performing sputtering, the a-axes and b shafts of a crystallographic axis of YSZ which are formed on a base material 1 are mutually turned in the same orientation, and can carry out orientation within a field along a field parallel to the top (membrane formation side) of a base material 1. [of a polycrystal thin film]

[0021] Here, as a result of an ion beam's flipping off the bad atom of the list [many] of these although both the good atom of the good stacking tendency of a list and the atom of the bad status of the bad stacking tendency of a list tend to accumulate in the initial stage of atomic deposition if the atom is deposited on the base material of usual non-orientation, irradiating an ion beam, especially in the initial stage of deposition, a membrane formation rate becomes bad. however, the atom of YSZ which it is going to come out of and is going to deposit on this base material 1 what [whose] is used in this gestalt is the base material 1 which raised the stacking tendency as a recrystallization texture beforehand The result which is going to carry out orientation better than the case where it is going to deposit on a non-orientation base material, Since the rate of the atom which exists in the good stable position of a stacking tendency becomes high, it becomes easy to deposit the good atom of the good stacking tendency of a list in the initial stage of deposition and a membrane formation rate improves, the polycrystal thin film 2 as a good interlayer of a stacking tendency generates early.

[0022] And if it forms by the forming [membranes] methods, such as sputtering and a laser vacuum deposition, on the polycrystal thin film 2 with which the laminating of the oxide-superconductivity layer 4 was carried out on the polycrystal thin film 2 formed as mentioned above, for example, the grain-boundary inclination was arranged with a sufficient precision as mentioned above, it will grow epitaxially and crystallize so that the oxide-superconductivity layer 4 by which a laminating is carried out on this polycrystal thin film 2 may also be adjusted in the stacking tendency of the polycrystal thin film 2. Therefore, the oxide-superconductivity layer 4 formed on the aforementioned polycrystal thin film 2 does not almost have turbulence in a crystal stacking tendency, the c axis which seldom passes the electrical and electric equipment in the thickness orientation of a base material 1 carries out orientation in

each of the crystal grain which constitutes this oxide-superconductivity layer 4, and aaxes or b shafts are carrying out orientation in the length orientation of a base material
1. Therefore, the obtained oxide-superconductivity layer is excellent in the quantum
associativity in the grain boundary, since there is almost no degradation of a
superconductivity property in the grain boundary, it becomes easy to pass the
electrical and electric equipment in the length orientation of a base material 1, and the
critical current density of the same grade as the oxide-superconductivity layer which
forms on MgO or the single crystal base material of SrTO3, and is obtained high
enough is obtained.

[0023] By the way, as shown in drawing 2, after forming the polycrystal thin film 2 on a base material 1, the polycrystal thin film 6 of further the product made from the same material may be formed on the polycrystal thin film 2 by the usual spatter (the spatter and the bias spatter method do not perform ion beam assistance) which is not the IBAD method, and the interlayer of two-layer structure may be formed. Here, if the polycrystal thin film 6 is formed on the good polycrystal thin film 2 of the crystal stacking tendency by the IBAD method, since the polycrystal thin film 6 grows epitaxially to the polycrystal thin film 2 and grows easily, it can also make high enough the crystal stacking tendency of the polycrystal thin film 6. thus, the oxide superconductivity of the structure shown in drawing 2 by forming the oxidesuperconductivity layer 4 on it while it can obtain easily the interlayer (thing of the thickness of the part which doubled the polycrystal thin film 2 and the polycrystal thin film 6) of thickness sufficient in the type to carry out where the fault of the IBAD method a membrane formation speed is slow is compensated and polycrystal basematerial 3' equipped with the polycrystal thin films 2 and 6 of sufficient thickness can be obtained, if it becomes -- a conductor can be obtained [0024]

[Example]

(Example 1) This metal tape was processed in thickness of 80 micrometers an oppressive total with the number pass of hot rolling manipulations (600 degrees C) using the pressure roll of a cemented carbide using the metal tape with a thickness [which consists of Hastelloy A (nickel 58%, Mo20%, Mn2.0%, Fe20%)] of 1mm. Then, heat treatment which cools this metal tape after 5 hour heating at 1500 degrees C more than a recrystallizing temperature was performed, and the metal tape base material which has a recrystallization texture was obtained. The average of the surface roughness of the metal tape after this rolling was **20nm or less. Then, the manufacturing installation of the polycrystal thin film of a configuration of being shown in drawing 3 was used, vacuum length of the interior of a membrane formation processing container of this manufacturing installation was carried out with the rotary pump and the cryopump, and it decompressed to 3.0x10-4 toll. A target uses the thing made from YSZ (stabilized zirconia). Moreover, spatter voltage 1000V, Set the degree of incident angle of the ion beam generated from 100mA of spatter currents, and the ion source as 55 degrees to the normal of the membrane formation side of a base material, and are set the assistant voltage of the ion source as 300V, and the current of the ion source is set as 60mA. While making the constituent particle of a target deposit on a base material, the ion beam was irradiated and the polycrystal thin film of YSZ of the shape of a layer with a thickness of 0.5 micrometers was formed over 1 hour. [0025] The result which performed the X-ray diffraction examination by the theta-

2theta method for having used CuK alpha rays about the polycrystal thin film of obtained YSZ, The peak of the field (200) of YSZ or (400) a field accepts, and that in which the field (100) of the polycrystal thin film of YSZ is carrying out orientation along the field parallel to a base-material front face can be presumed. It became clear that the polycrystal thin film of YSZ carries out orientation of the c axis at right angles to the membrane formation side of a base material, and is formed. [0026] Next, it measured whether in this polycrystal thin film of YSZ, the a-axis or b shaft of a polycrystal thin film of YSZ would carry out orientation. For the measurement, as shown in drawing 6, while an X-ray is irradiated at an angle theta 1 at the polycrystal thin film 2 formed on the base material 1 In the vertical plane containing an incidence X-ray, install the X-ray counter 58 in the position of the angle of 2theta1 to an incidence X-ray, and the value of level angle phi to the vertical plane containing an incidence X-ray is changed suitably. That is, the stacking tendency of the a-axes of the polycrystal thin film 2 or b shafts was measured by measuring the diffraction strength obtained when only angle-of-rotation phi makes it rotate as a base material 1 is shown in the arrow head in drawing 6. Consequently, when phi was made into 90 degrees and 0 times in the case of the polycrystal thin film of this example, the peak of the field (111) of YSZ appeared every 90 degrees to angle-ofrotation phi. This is equivalent to the peak (011) of YSZ within a substrate side, and it became clear that the a-axes or b shafts of a polycrystal thin film of YSZ is carrying out orientation.

[0027] Furthermore, the crystal stacking tendency in each crystal grain of the polycrystal layer of the polycrystal thin film of obtained YSZ was measured. In this measurement, when X-ray diffraction was performed by the technique previously explained on the basis of drawing 6, the diffraction peak at the time of setting the angle of phi as the value of a unit once to -ten - +10 degrees was measured. From the result, although the diffraction peak of the polycrystal thin film of obtained YSZ appeared in less than **three - five grain-boundary inclinations, having disappeared made it clear at **8 - 10 degrees. Therefore, having fitted in less than 10 degrees clear the grain-boundary inclination of the crystal grain of the obtained polycrystal thin film, and it became clear to have a good stacking tendency. [0028] next, the polycrystal thin film top of the above YSZ -- laser vacuum evaporationo equipment -- using -- an oxide-superconductivity layer with a thickness of 1.0 micrometers -- forming -- oxide superconductivity -- the conductor was produced the target with which this laser vacuum evaporationo equipment is equipped ***** -- Y1.0Ba2.0Cu3.0O7-x -- the target which consists of an oxides superconductors of composition was used After having introduced oxygen into the interior after decompressing the interior of a membrane formation processing room to 1x10-6 toll, and considering as 2x10-3 toll, laser vacuum evaporationo was performed. ArF laser with a wavelength of 193nm was used as laser for target vaporization. after this membrane formation and 400 degreeC -- for 60 minutes and the inside of the oxygen ambient atmosphere -- setting -- a thin film -- heat-treating -oxide superconductivity -- the conductor was obtained [0029] this oxide superconductivity -- as a result of cooling a conductor to 77K by liquid nitrogen and measuring a critical current density by 4 terminal method on condition that external magnetic field 0T (tesla), critical-current-density =8.2x10A/cm2 were shown, and it has checked demonstrating a very excellent

superconductivity property

[0030] (Example of a comparison) Instead of the stacking-tendency metal tape which has the texture of the aforementioned example, although the completely same processing as an example was performed using the metal tape made from a Hastelloy of non-orientation into which it is not processed and the interlayer of YSZ with a thickness of 0.5 micrometers was formed on the base-material tape, in order to form an interlayer with a thickness of 0.5 micrometers, the same conditions as the above took 5 hours. this oxide superconductivity -- although it has checked critical-current-density =8.0x10A/cm2 being shown, and demonstrating an excellent superconductivity property equivalent to a previous example as a result of cooling a conductor 77K by liquid nitrogen and measuring a critical current density by 4 terminal method on condition that external magnetic field 0T (tesla), when the non-orientation metal tape was used, it became clear that an interlayer's membrane formation takes the time when it is 5 times many as this [0031]

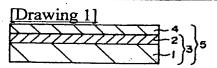
[Effect of the Invention] If it is in a stacking-tendency polycrystal base material according to claim 1 as explained above, since it is the stacking-tendency polycrystal base material to which it comes to provide a base material and a stacking-tendency polycrystal interlayer, and the laminating of the stacking-tendency stratum functionale is carried out, it consists of a high degree-of-hardness metal of the high-melting point of cubic system and it considers as a rolling texture, what has the good polycrystal interlayer of a stacking tendency easily on the good base material of the stacking tendency made into the rolling texture is obtained. And since orientation also of the crystal stacking tendency of the stacking-tendency stratum functionale formed on a stacking-tendency polycrystal interlayer can be easily carried out in accordance with a stacking-tendency polycrystal interlayer, the stacking-tendency stratum functionale which was excellent in the crystal stacking tendency as a result can be obtained. Moreover, since a base material consists of a high degree-of-hardness metal of the high-melting point of cubic system, its intensity is high and it can be applied also to the intended use on which mechanical stress tends to act.

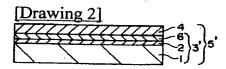
[0032] moreover, a superconductivity according to claim 2, if it is in a conductor Since it is characterized by coming to provide the base material which consists of a high degree-of-hardness metal of the high-melting point of cubic system, and was made into the rolling texture, the stacking-tendency polycrystal interlayer formed on this base material, and the oxide-superconductivity layer formed on this stackingtendency polycrystal interlayer While what has the good polycrystal interlayer of a stacking tendency easily on the good base material of the stacking tendency made into the rolling texture is obtained The crystal stacking tendency of the oxidesuperconductivity layer formed on a stacking-tendency polycrystal interlayer can also obtain the oxide-superconductivity layer which could be made to carry out orientation easily in accordance with a stacking-tendency polycrystal interlayer, was excellent in the crystal stacking tendency as a result, and was excellent in the superconductivity property. moreover, magnetic field application intended use, such as a superconductive magnet, a superconductivity power generation machine, etc. on which an intensity is high and mechanical stress tends to act since a base material consists of a high degree-of-hardness metal of the high-melting point of cubic system. -- also receiving -- an intensity ---like -- it is applicable satisfactory

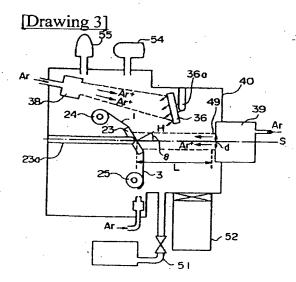
[0033] Next, in invention according to claim 3, it can consider as a recrystallization texture by performing strip processing of 90% or more of workabilities at the temperature more than a recrystallizing temperature, and forming a base material to the material which consists of a high degree-of-hardness metal of the high-melting point of cubic system, and can consider as the good base material of a crystal stacking tendency. By and the thing for which an ion beam is irradiated from across and a stacking-tendency polycrystal interlayer is formed at the same time it makes an interlayer's constituent particle deposit on this base material In case it leaves alternatively only the good atom of the good crystal stacking tendency of a list and it is made to deposit, removing the atom which is made to deposit the atom which should constitute a stacking-tendency polycrystal thin film on a base material, and is in the bad unstable position of a list by the ion beam Since it can double with the stacking tendency of a stacking-tendency base material by the initial stage of deposition and an atom can be made to deposit with the priority to the good status of the good stacking tendency of a list, the good stacking-tendency polycrystal interlayer of a stacking tendency can be formed in time when it is shorter than the former so that the stacking tendency of a base material may be met. moreover, the oxide superconductivity which was excellent in the superconductivity property which forms an oxide-superconductivity layer, and which was excellent in the transition-current property as a result since it had by the good crystal stacking tendency on the stackingtendency polycrystal interlayer and the oxide-superconductivity layer was formed when becoming on the stacking-tendency polycrystal interlayer -- a conductor can be manufactured in time when it is shorter than the conventional technique, and there is an effect which can improve manufacture luminous efficacy

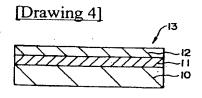
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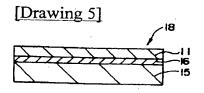
DRAWINGS

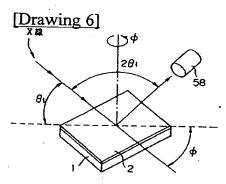




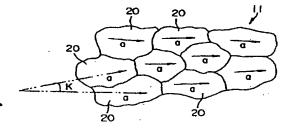








[Drawing 7]



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(71) [Applicant]

[Identification Number] 000005186.

[Name] Fujikura, Inc.

[Address] 1-5-1, Kiba, Koto-ku, Tokyo.

(72) [Inventor(s)]

[Name] Iijima Yasuhiro.

[Address] 1-5-1, Kiba, Koto-ku, Tokyo Inside of Fujikura, Inc.

(72) [Inventor(s)]

[Name] Hosaka Truth child.

[Address] 1-5-1, Kiba, Koto-ku, Tokyo Inside of Fujikura, Inc.

(72) [Inventor(s)]

[Name] Sadakata Nobuyuki.

[Address] 1-5-1, Kiba, Koto-ku, Tokyo Inside of Fujikura, Inc.

(72) [Inventor(s)]
[Name] Saito **.
[Address] 1-5-1, Kiba, Koto-ku, Tokyo Inside of Fujikura, Inc.
(72) [Inventor(s)]
[Name] Tanabe Nobuo.
[Address] 1-5-1, Kiba, Koto-ku, Tokyo Inside of Fujikura, Inc.
(74) [Attorney]
[Patent Attorney]
[Name] Shiga Masatake (besides three persons)

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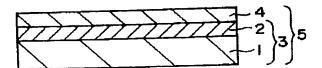
Summary.

(57) [Abstract]

[Technical problem] the oxide superconductivity equipped with a base material with high intensity while this invention aimed at the ability to be able to make the polycrystal thin film excellent in a crystal stacking tendency deposit at a membrane—formation speed quick than before on a base material and it had the polycrystal thin film which formed the high polycrystal thin film of a crystal stacking tendency on it using a base material with high intensity and degree of hardness, and is excellent in a stacking tendency — aiming at technical offer which manufactures a conductor

[Means for Solution] this invention is the stacking-tendency polycrystal base material 3 to which it comes to provide a base material 1 and the stacking-tendency polycrystal interlayer 2, and the laminating of the stacking-tendency functional layer 3 is carried out further, consists of a high degree-of-hardness metal of the high-melting point of cubic system, and is characterized by considering as rolling texture.

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CLAIMS

[Claim(s)]

[Claim 1] The stacking—tendency polycrystal base material which is a stacking—tendency polycrystal base material to which it comes to provide a base material and a stacking—tendency polycrystal interlayer, and the laminating of the stacking—tendency functional layer is carried out further, and is characterized by for the aforementioned base material having consisted of a high degree—of—hardness metal of the high—melting point of cubic system, and making it into rolling texture.

[Claim 2] the oxide superconductivity which consists of a high degree—of—hardness metal of the high—melting point of cubic system, possesses the base material made into rolling texture, the stacking—tendency polycrystal interlayer formed on this base material, and the oxide superconductivity layer formed on this stacking—tendency polycrystal interlayer, and is characterized by the bird clapper —— a conductor

[Claim 3] the oxide superconductivity characterized by to carry out the laminating of the oxide-superconductivity layer on this stacking-tendency polycrystal interlayer while heat treatment heated to the temperature more than a recrystallizing temperature is performed, and forming a base material, irradiating an ion beam from across and forming a stacking-tendency polycrystal interlayer to the material which consists of a high degree-of-hardness metal of the high-melting point of cubic system at the same time it makes an interlayer's constituent particle deposit on this base material after performing strip processing of 90% or more of workability — the manufacture method of a conductor

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DETAILED DESCRIPTION

[Detailed Description of the Invention] [0001]

[The technical field to which invention belongs] this invention relates to the thing equipped with the interlayer excellent in the crystal stacking tendency on base materials, such as the shape of a tape, and the structure further equipped with stacking—tendency stratum functionale, such as an oxide superconductivity layer with an excellent superconductivity property, on it, and its manufacture method. [0002]

[Description of the Prior Art] although the oxides superconductors become and discovered at recent years are outstanding superconductors which show the critical temperature exceeding liquid nitrogen temperature -- present and this kind of oxides superconductors -- practical superconductivity -- in order to use it as a conductor, the trouble which should solve various exists One of the trouble of the is a problem of a low in the critical current density of oxides superconductors. [0003] Although the problem of a low in the critical current density of oxides superconductors is the cause with big an anisotropy electric into the crystal of oxides superconductors itself existing and especially oxides superconductors tend to pass the electrical and electric equipment to a shaft orientations and b shaft orientations of the crystallographic axis, it is known that it will be hard to pass the electrical and electric equipment to c shaft orientations. such a viewpoint to oxides superconductors -- a base-material top -- forming -- this -- superconductivity -- in order to use it as a conductor, it is necessary to form the oxides superconductors of the good state of a crystal stacking tendency on a base material, to make the orientation of the a-axis or b-axis of the crystal of oxides superconductors carry out in the direction which is going to pass the electrical and electric equipment moreover, and to make the orientation of the c axis of oxides superconductors carry out in the direction of other [0004] By the way, in order to use oxides superconductors as a conductor, it is

[0004] By the way, in order to use oxides superconductors as a conductor, it is necessary to form the good oxide superconductivity layer of a crystal stacking tendency on the base material of long pictures, such as the shape of a tape. However, as for the metal tape itself, if an oxide superconductivity layer is directly formed on base materials, such as a metal tape, since it differs from oxides superconductors greatly, the crystal structure cannot form the good oxide superconductivity layer of a crystal stacking tendency at all by the polycrystalline

substance, either. And since a diffusion reaction arises between a metal tape and an oxide superconductivity layer with heat treatment performed in case an oxide superconductivity layer is formed, the crystal structure of an oxide superconductivity layer collapses and there is a problem on which a superconductivity property deteriorates. Then, this invention persons form the polycrystal thin films (interlayer) 11, such as an yttrium stabilized zirconia (YSZ), on the base material 10 as shown in drawing 4 which consists of metal tapes, such as a Hastelloy tape. On this polycrystal thin film 11, critical temperature is about 90K also in oxides superconductors, the superconductivity which excelled [form / the superconductivity layer 12 of the Y1Ba2Cu3Ox system excellent in the stability which can be used in liquid nitrogen (77K)] in the superconductivity property -- various attempts which manufacture a conductor 13 are performed Out of such an attempt, previously, this invention persons are performing patent application in Japanese Patent Application No. No. 126836 [three to], Japanese Patent Application No. No. 126837 [three to], Japanese Patent Application No. No. 205551 [two to], Japanese Patent Application No. No. 13443 [four to], Japanese Patent Application No. No. 293464 [four to], Japanese Patent Application No. No. 210777 [five to], etc., in order to form the polycrystal thin film excellent in the crystal stacking tendency, or in order to obtain the superconductivity tape which was excellent in the superconductivity property. [0005] In case the constituent particle of the target prepared in the membrane formation processing container is made to deposit on the base material of the shape of a tape, such as a Hastelloy tape, according to the technology indicated by such patent application It is made to deposit, irradiating the ion beam which made it generate from the ion source from across to the normal of the membrane formation side of a base material with a certain specific degree of incident angle (50 - 60 degrees). By the method (ion beam assistant vacuum deposition : the IBAD method) of forming a polycrystal thin film on a base material, the polycrystal thin film excellent in the crystal stacking tendency can be formed. The detailed crystal grain which has the crystal structure of cubic system this polycrystal thin film in large numbers Come to carry out junction unification through the grain boundary, and orientation of the c axis of the crystallographic axis of each crystal grain is carried out right-angled to the upper surface (membrane formation side) of a base material. The a-axes and b-axes of a crystallographic axis of each crystal grain are mutually turned in the same direction, and orientation within a field is carried out along the field parallel to the membrane formation side of a base material. Moreover, the a-axes (or b-axis) of each crystal grain 20 which constitutes the polycrystal thin film 11 as shown in drawing 6 are arranging and carrying out orientation of those angles (grain-boundary inclination K) to make to about 30 or less degrees, and the thing which forms the superconductivity layer of a YBaCuO system by the laser vacuum deposition etc. on the polycrystal thin film excellent in this crystal stacking tendency further and which was excellent also in the crystal stacking tendency of an oxide superconductivity layer when becoming -- becoming -- thereby -- 77K -- oxide superconductivity with as high critical current density as two or more 105 A/cm -- a conductor can be obtained [0006] by the way, the oxide superconductivity manufactured using the IBAD

method explained previously — the oxide superconductivity of the structure which makes the stacking—tendency metal tape which consists of nickel or Ag as shown in drawing 5 other than a conductor 13 a base material 15, and comes to carry out the laminating of the reaction prevention interlayer 16 and the oxide superconductivity layer 17 on it — the conductor 18 is known this kind of oxide superconductivity — in a conductor, it is the structure which was going to perform strip processing to the metal tape which consists of nickel or Ag, was going to raise the stacking tendency systematic as a texture for the organization to it, and was going to raise the crystal stacking tendency of a reaction prevention interlayer and an oxide superconductivity layer to it based on this stacking—tendency metal tape

[0007]

[Problem(s) to be Solved by the Invention] the oxide superconductivity by the IBAD method which this invention persons developed -- although the conductor 13 was known as what shows the outstanding critical current density, in order to form the polycrystal thin film 11 used as an interlayer, it required time and had the problem that manufacture efficiency was bad In case the IBAD method deposits the atom of YSZ, irradiating an ion beam from across, this By the spatter effect of an ion beam, flip off the bad atom of the bad stacking tendency of a list unstable in energy, and it is removed. Since it is the technology in which it obtains the good polycrystal thin film of a stacking tendency by leaving alternatively only the good atom of the good stacking tendency of a list stable in energy, and making it deposit In order for the deposition efficiency of the atom by the spatter to fall, compared with membrane formation by the usual spatter, the membrane formation rate originates in the bad thing. In addition, as a result of this invention persons' observing the state of atomic deposition here, especially advance of deposition of the atom by the IBAD method was slow in the first stage, and after the good atom of the stacking tendency of a certain amount of thickness accumulated, the comparatively quick thing made it clear. Although the atom of the bad state of the bad stacking tendency of especially a list tends to deposit this in the initial stage of atomic deposition, as a result of an ion beam's flipping off the bad atom of the list of these many, especially in the initial stage of deposition, a membrane formation rate is bad, and after the stacking tendency has been ready to some extent and atomic deposition advances, it is thought that the atom deposited after that is because the establishment deposited in a good stacking tendency is high. This invention persons reached the invention in this application this time for the purpose of the ability to make the polycrystal thin film excellent in the crystal stacking tendency deposit at a membrane formation speed quicker than before on a base material based on such an IBAD method.

[0008] next, the former using the base material 15 of a stacking-tendency metal tape as shown in drawing 5 — the oxide superconductivity of structure — since a conductor 18 was the structure using the texture by rolling of a base material 15, comparatively soft base materials (Ag is Hv=20-30 and nickel is about Hv=80), such as nickel and Ag, needed to be used for it here — superconductivity — since the application technology of a conductor is applied to the member on which mighty magnetism and big mechanical power act like a super-conductive magnet or

a superconductivity generator, although what has a degree of hardness high as much as possible and intensity high as much as possible is desirable as for a base material, it has a possibility of becoming the shortage of intensity, by nickel or Ag Moreover, since it has ferromagnetism in itself, nickel has an inapplicable problem in the base material of magnetic field application, the oxide superconductivity equipped with the base material with high intensity while this invention persons had the polycrystal thin film which formed the high polycrystal thin film of a crystal stacking tendency on it in view of the problem of structure using the base material with high intensity and degree of hardness such conventionally, and was excellent in the stacking tendency — it aims at technical offer which manufactures a conductor

[0009] [Means for Solving the Problem] It is characterized by being the stacking-tendency polycrystal base material to which it comes to provide a base material and a stacking-tendency polycrystal interlayer, and the laminating of the stackingtendency stratum functionale is carried out, and for the base material having consisted of a high degree-of-hardness metal of the high-melting point of cubic system, and making this invention into rolling texture, in order to solve the aforementioned technical problem. Furthermore, this invention consists of a high degree-of-hardness metal of the high-melting point of cubic system, and it comes to provide the base material made into rolling texture, the stacking-tendency polycrystal interlayer formed on this base material, and the oxide superconductivity layer formed on this stacking tendency polycrystal interlayer. Next, it is characterized by carrying out the laminating of the oxide superconductivity layer on this stacking-tendency polycrystal interlayer while this invention performs heat treatment heated to the temperature more than a recrystallizing temperature, forms a base material, irradiates an ion beam from across and forms a stackingtendency polycrystal interlayer to the material which consists of a high degree-ofhardness metal of the high-melting point of cubic system at the same time it makes an interlayer's constituent particle deposit on this base material after performing strip processing of 90% or more of workability.

[Embodiments of the Invention] the oxide superconductivity to which drawing 1 comes to carry out the laminating of the oxide—superconductivity layer to the polycrystal base material concerning this invention — what shows the cross—section structure of 1 operation gestalt of a conductor — it is — the oxide superconductivity of this operation gestalt — the laminating of the interlayer (stacking—tendency polycrystal thin film) 2 is carried out to the upper surface of the base materials 1, such as the shape of a tape, the polycrystal base material 3 is constituted and the oxide—superconductivity layer (stacking—tendency stratum functionale) 4 carries out the laminating of the conductor 1 to the upper surface of this the aforementioned base material 1 — a nickel—Cr system (concrete — Hastelloy B of an nickel—Cr—Fe—Mo system —) W—Mo systems, such as C and X, a Fe—Cr system (for example, austenite stainless steel), The nonmagnetic alloy beyond Hv=150 of the cubic system represented by material, such as a Fe—nickel system (for example, thing of a nonmagnetic composition system), to a bird clapper

is desirable. 90% or more of hot rolling processing is given to the alloy of these systems, heat treatment of 5 hours is performed at the temperature of several hours, for example, 1500 degrees C, further after that with the temperature more than a recrystallizing temperature (1200–1500 degrees C), and it considers as a recrystallization texture. Moreover, as for the front face of a base material 1, it is desirable that the value of full width at half maximum (full width at half maximum) which shows **10–20nm of surface roughness and the stacking tendency within a field is made into about 10 degrees.

[0011] The aforementioned Hastelloy is known for making composition of Remainder nickel into a subject Cr:1-23.0%, Fe:4-20%, Mo:8-30%, Co:0.5-2.5%, and W:0.2 to 4.5%, and its degree of hardness of the range of Hv=200-400 is high. Each alloy of the nickel-Cr system represented by these Hastelloies is an alloy of a high degree of hardness, and it comes to show a good crystal stacking tendency, being used as a texture by being heat-treated after 90% or more of strong processing above a recrystallizing temperature. The aforementioned interlayer (stacking-tendency polycrystal thin film) 2 consists of an yttrium stabilized zirconia (YSZ), a cerium oxide (CeO2), a yttrium oxide (Y2O3), etc., and forms membranes on a base material 1 by the above-mentioned IBAD method in which this invention persons are doing patent application.

[0012] Drawing 3 is drawing showing an example of the manufacturing installation of the polycrystal thin film used suitable for the manufacture of an interlayer 2 formed on a base material 1. The base-material electrode holder 23 which can be heated to request temperature while the manufacturing installation of this polycrystal thin film supports the tape-like base material 1, The base-material sending-out bobbin 24 for sending out the tape-like base material 1 on the basematerial electrode holder 23, The base-material winding bobbin 25 for rolling round the tape-like base material 1 in which the polycrystal thin film was formed, The target 36 of the tabular by which opposite arrangement was carried out with the predetermined interval in the slanting upper part of the aforementioned basematerial electrode holder 23, The spatter beam irradiation equipment 38 arranged towards the undersurface of a target 36 in the slanting upper part of this target 36 (spatter means), The side of the aforementioned base-material electrode holder 23 is countered with a predetermined interval, and the ion source 39 which estranged with the aforementioned target 36 and has been arranged has outline composition contained in the membrane formation processing container 40 in which evacuation is possible.

[0013] The aforementioned base-material electrode holder 23 equips the interior with a heating heater, and can heat now the base material 1 of the shape of a tape sent out on the base-material electrode holder 23 to desired temperature if needed. This base-material electrode holder 23 is attached in base material 23a free [rotation] by the pin etc., and can adjust the degree of tilt angle now. Such a base-material electrode holder 23 is arranged in the optimal irradiation field of the ion beam irradiated from the ion source 39 in the membrane formation processing container 40.

[0014] In the manufacturing installation of the polycrystal thin film of this example, the tape-like base material 1 can be continuously sent out on the base-material

electrode holder 23 from the aforementioned base-material sending-out bobbin 24, and continuation membrane formation of the base material 1 by which the polycrystal thin film was formed in the aforementioned optimal irradiation field can be carried out now on a base material 1 by rolling round with the base-material winding bobbin 25. This base-material winding bobbin 25 is arranged out of the aforementioned optimal irradiation field.

[0015] The aforementioned target 36 is for forming the polycrystal thin film made into the purpose, and the thing of the same composition as the polycrystal thin film of the target composition or approximation composition etc. is used for it. What is necessary is not to restrict to these, although the zirconia (YSZ) specifically stabilized by MgO or Y2O3, a cerium oxide (CeO2), a yttrium oxide (Y2O3), etc. are used as a target 36, and just to use suitably the target corresponding to the polycrystal thin film which it is going to form. Such a target 36 is attached in target base material 36a free [rotation] by the pin etc., and can adjust the degree of tilt angle now. The aforementioned spatter beam irradiation equipment (spatter means) 38 is equipped with the grid for containing an evaporation source to the interior of a container, pulling out inside near the evaporation source, and applying voltage to it, is constituted, irradiates an ion beam to a target 36, and can turn and drive the constituent particle of a target 36 in a base material 22.

[0016] It is the thing of the same composition as the spatter beam irradiation equipment 38 and abbreviation, and the aforementioned ion source 39 contains an evaporation source inside a container, it is equipped with the grid for pulling out near the evaporation source and applying voltage, and is constituted. And it is equipment which a part of atom generated from the aforementioned evaporation source or molecule is ionized, and it controls by the electric field which generated the ionized particle in the grid, and is irradiated as an ion beam. As shown in drawing 3, the aforementioned ion source 39 has the medial-axis line S, made it incline to the membrane formation side (front face) of the base material 1 on the base-material electrode holder 23 with the degree theta of incident angle (angle of the perpendicular (normal) H of a base material 1, and a center line S to make), and has countered. although this degree theta of incident angle has the desirable range of 50 - 60 degrees -- more -- desirable -- the range of 55 - 60 degrees -- it is just over or below 55 degrees most preferably Therefore, the ion source 39 is arranged so that it may have with the degree theta of incident angle to which the normal H of the membrane formation side of a base material 22 is received and an ion beam can be irradiated.

[0017] In addition, although the ion beam of rare gas, such as helium+, Ne+, Ar+, Xe+, and Kr+, or the mixed ion beam of they and oxygen ion is sufficient as the ion beam which irradiates a base material 22 with the aforementioned ion source 39 when forming the interlayer 2 of YSZ, when forming CeO2, the mixed ion beam of Xe+, Kr+, or these 2 element is used for it. Moreover, controlled-atmosphere sources of supply, such as a chemical cylinder, are connected with the rotary pump 51 for changing the inside of this container 40 into low voltage states, such as a vacuum, and the cryopump 52 at the aforementioned membrane formation processing container 40, respectively, and it can be made the inert gas atmosphere which is in low voltage states, such as a vacuum, about the interior of the

membrane formation processing container 40, and contains the inert gas atmosphere or oxygen of argon gas or others now. Furthermore, the current density metering device 55 for measuring the current density of the ion beam in this container 40 and the pressure gage 55 for measuring the pressure in the aforementioned container 40 are attached in the aforementioned membrane formation processing container 40.

[0018] Next, the case where the polycrystal thin film of YSZ is formed on the tape-like base material 1 using the manufacturing installation of the aforementioned composition is explained. In order to form a polycrystal thin film on the tape-like base material 22, while carrying out vacuum length of the interior of the membrane formation processing container 40 which has contained the base material 22 using the target 36 which consists of YSZ and considering as reduced pressure atmosphere, a base material 1 is sent out to the base-material electrode holder 23 at the rate of predetermined from the base-material sending-out bobbin 24, and the ion source 39 and the spatter beam irradiation equipment 38 are

operated further.

[0019] If an ion beam is irradiated from the spatter beam irradiation equipment 38 to a target 36, the constituent particle of a target 36 will be begun to beat, and it will come flying on a base material 1. And from the ion source 39, for example, the mixed ion beam of Ar ion and oxygen ion is irradiated, the polycrystal thin film of desired thickness is formed, and the base material 1 of the shape of a tape after membrane formation is rolled round in the base-material winding bobbin 25 at the same time it makes the constituent particle begun to beat from the target 36 deposit on the base material 1 sent out on the base-material electrode holder 23. [0020] The degree theta of incident angle at the time of irradiating an ion beam here has the desirable range of 50 - 60 degrees, and it is just over or below 55 degrees more preferably. If theta is made into 90 degrees here, although orientation of the c axis of a polycrystal thin film is carried out right-angled to the membrane formation side on a base material 22, since a field (111) stands on the membrane formation side of a base material 22, it is not desirable. Moreover, if theta is made into 30 degrees, a polycrystal thin film will not carry out even c axis orientation. If ion beam irradiation is carried out with the degree of incident angle of the above desirable ranges, the field (100) of the crystal of a polycrystal thin film will come to stand. By performing sputtering, performing ion beam irradiation with such a degree of incident angle, the a-axes and b-axes of a crystallographic axis of YSZ which are formed on a base material 1 are mutually turned in the same direction, and can carry out orientation within a field along a field parallel to the upper surface (membrane formation side) of a base material 1. [of a polycrystal thin film]

[0021] Here, if the atom is deposited on the base material of the usual nonorientation, irradiating an ion beam, although both the good atom of the good stacking tendency of a list and the atom of the bad state of the bad stacking tendency of a list tend to accumulate in the initial stage of atomic deposition, as a result of an ion beam's flipping off the bad atom of the list of these many, especially in the initial stage of deposition, a membrane formation rate becomes bad. however, the atom of YSZ out of which it is going to come and which it is

going to deposit on this base material 1 what [whose] is used in this gestalt is the base material 1 which raised the stacking tendency as a recrystallization texture beforehand The result which is going to carry out orientation better than the case where it is going to deposit on a non-orientation base material, Since the rate of the atom which exists in the good stable position of a stacking tendency becomes high, it becomes easy to deposit the good atom of the good stacking tendency of a list in the initial stage of deposition and a membrane formation rate improves, the polycrystal thin film 2 as a good interlayer of a stacking tendency generates early. [0022] And if it forms by the forming-membranes methods, such as sputtering and a laser vacuum deposition, on the polycrystal thin film 2 with which the laminating of the oxide superconductivity layer 4 was carried out on the polycrystal thin film 2 formed as mentioned above, for example, the grain-boundary inclination was arranged with a sufficient precision as mentioned above, it will grow epitaxially and crystallize so that the oxide superconductivity layer 4 by which a laminating is carried out on this polycrystal thin film 2 may also be adjusted in the stacking tendency of the polycrystal thin film 2. Therefore, the oxide superconductivity layer 4 formed on the aforementioned polycrystal thin film 2 does not almost have disorder in a crystal stacking tendency, the c axis which cannot pass the electrical and electric equipment easily in the thickness direction of a base material 1 carries out orientation in each of the crystal grain which constitutes this oxide superconductivity layer 4, and a-axes or b-axes are carrying out orientation in the length direction of a base material 1. Therefore, since the obtained oxide superconductivity layer is excellent in the quantum unity in the grain boundary and does not almost have degradation of the superconductivity property in the grain boundary, it becomes easy to pass the electrical and electric equipment in the length direction of a base material 1, and the critical current density of the same grade as the oxide superconductivity layer which forms on MgO or the single crystal base material of SrTO3, and is obtained high enough is obtained. [0023] By the way, as shown in drawing 2, after forming the polycrystal thin film 2 on a base material 1, the polycrystal thin film 6 of further the product made from the same material may be formed on the polycrystal thin film 2 by the usual spatter (the spatter and the bias spatter method do not perform ion beam assistance) which is not the IBAD method, and the interlayer of two-layer structure may be formed. Here, if the polycrystal thin film 6 is formed on the good polycrystal thin film 2 of the crystal stacking tendency by the IBAD method, since the polycrystal thin film 6 will grow epitaxially to the polycrystal thin film 2 and will grow easily, also let the crystal stacking tendency of the polycrystal thin film 6 be a thing high enough. thus, the oxide superconductivity of the structure shown in drawing 2 by forming the oxide superconductivity layer 4 on it while being able to obtain easily the interlayer (thing of the thickness of the part which doubled the polycrystal thin film 2 and the polycrystal thin film 6) of thickness sufficient in the form to carry out where the fault of the IBAD method membrane formation speed is slow is compensated and being able to obtain polycrystal base-material 3' equipped with the polycrystal thin films 2 and 6 of sufficient thickness, if it becomes -- a conductor can be obtained [0024]

[Example]
(Example 1) This metal tape was processed into 80 micrometers in thickness an oppressive total with the number path of hot rolling processings (600 degrees C) using the pressure roll of cemented carbide using the metal tape with a thickness of 1mm it is thin from Hastelloy A (nickel58%, Mo20%, Mn2.0%, Fe20%). Then, heat treatment which cools this metal tape after 5-hour heating at 1500 degrees C more than a recrystallizing temperature was performed, and the metal tape base material which has a recrystallization texture was obtained. The average of the surface roughness of the metal tape after this rolling was **20nm or less. Then, the manufacturing installation of the polycrystal thin film of composition of being shown in drawing 3 was used, vacuum length of the interior of a membrane

formation processing container of this manufacturing installation was carried out with the rotary pump and the cryopump, and it decompressed to 3.0x10 to 4 torrs. A target uses the thing made from YSZ (stabilized zirconia). Moreover, spatter voltage 1000V, Set the degree of incident angle of the ion beam which makes it generate from 100mA of spatter current, and the ion source as 55 degrees to the normal of the membrane formation side of a base material, and are set the

assistant voltage of the ion source as 300V, and the current of the ion source is set as 60mA. While making the constituent particle of a target deposit on a base material, the ion beam was irradiated and the polycrystal thin film of YSZ of the shape of a film with a thickness of 0.5 micrometers was formed over 1 hour.

[0025] The result which performed the X diffraction examination by the theta-2theta method for having used CuK alpha rays about the polycrystal thin film of obtained YSZ, The peak of the field (200) of YSZ or (400) a field is accepted, and that in which the field (100) of the polycrystal thin film of YSZ is carrying out orientation along the field parallel to a base-material front face can be presumed. It

became clear that the polycrystal thin film of YSZ carries out orientation of the c axis at right angles to the membrane formation side of a base material, and is formed.

[0026] Next, it measured whether in this polycrystal thin film of YSZ, the a-axis or b-axis of a polycrystal thin film of YSZ would carry out orientation. For the measurement, as shown in drawing 6, while irradiating an X-ray at an angle that 1 at the polycrystal thin film 2 formed on the base material 1 In the vertical plane containing an incidence X-ray, install the X-ray counter 58 in the position of the angle of 2theta1 to an incidence X-ray, and the value of the level angle phi to the vertical plane containing an incidence X-ray is changed suitably. That is, the stacking tendency of the a-axes of the polycrystal thin film 2 or b-axes was measured by measuring the diffraction strength obtained when only an angle of rotation phi makes it rotate as a base material 1 is shown in an arrow in drawing 6. Consequently, when phi was made into 90 degrees and 0 times in the case of the polycrystal thin film of this example, the peak of the field (111) of YSZ appeared every 90 degrees to the angle of rotation phi. This is equivalent to the peak (011) of YSZ within a substrate side, and it became clear that the a-axes or b-axes of a polycrystal thin film of YSZ is carrying out orientation.

[0027] Furthermore, the crystal stacking tendency in each crystal grain of the polycrystal layer of the polycrystal thin film of obtained YSZ was measured. In this

measurement, when an X diffraction was performed by the method previously explained based on drawing 6, the diffraction peak at the time of setting the angle of phi as the value of serration once to -ten - +10 degrees was measured. Although the diffraction peak of the polycrystal thin film of YSZ obtained from the result appeared in less than **three - five grain-boundary inclinations, having disappeared made it clear at **8 - 10 degrees. Therefore, having fitted in less than 10 degrees made clear the grain-boundary inclination of the crystal grain of the obtained polycrystal thin film, and it became clear to have a good stacking tendency.

[0028] next, the polycrystal thin film top of Above YSZ — laser vacuum evaporationo equipment — using — an oxide superconductivity layer with a thickness of 1.0 micrometers — forming — oxide superconductivity — the conductor was produced as the target with which this laser vacuum evaporationo equipment is equipped — Y1.0Ba2.0Cu 3.007-x — the target which consists of oxides superconductors of composition was used After having introduced oxygen into the interior after decompressing the interior of a membrane formation processing room to 1x10 to 6 torrs, and considering as 2x10 to 3 torrs, laser vacuum evaporationo was performed. ArF laser with a wavelength of 193nm was used as laser for target evaporation. after [this membrane formation] and 400 degreeC — for 60 minutes and the inside of oxygen atmosphere — setting — a thin film — heat-treating — oxide superconductivity — the conductor was obtained

[0029] this oxide superconductivity — as a result of cooling a conductor to 77K by liquid nitrogen and measuring critical current density by 4 terminal method on condition that external magnetic field 0T (tesla), critical—current—density =8.2x10 A/cm2 was shown, and it has checked demonstrating a very excellent superconductivity property

[0030] (Example of comparison) Instead of the stacking-tendency metal tape which has the texture of the aforementioned example, although the completely same processing as an example was performed using the metal tape made from a Hastelloy of non-orientation into which it is not processed and the interlayer of YSZ with a thickness of 0.5 micrometers was formed on the base-material tape, in order to form an interlayer with a thickness of 0.5 micrometers, the same conditions as the above took 5 hours. this oxide superconductivity — although it has checked critical-current-density =8.0x10 A/cm2 being shown, and demonstrating an excellent superconductivity property equivalent to a previous example as a result of cooling a conductor 77K by liquid nitrogen and measuring critical current density by 4 terminal method on condition that external magnetic field 0T (tesla), when the non-orientation metal tape was used, it became clear that an interlayer's membrane formation takes 5 times as many time as this [0031]

[Effect of the Invention] If it is in a stacking-tendency polycrystal base material according to claim 1 as explained above, since it is the stacking-tendency polycrystal base material to which it comes to provide a base material and a stacking-tendency polycrystal interlayer, and the laminating of the stacking-tendency functional layer is carried out, it consists of a high degree-of-hardness

metal of the high-melting point of cubic system and it considers as rolling texture, what has the good polycrystal interlayer of a stacking tendency easily on the good base material of the stacking tendency made into rolling texture is obtained. And since orientation also of the crystal stacking tendency of the stacking-tendency functional layer formed on a stacking-tendency polycrystal interlayer can be easily carried out according to a stacking-tendency polycrystal interlayer, the stackingtendency functional layer which was excellent in the crystal stacking tendency as a result can be obtained. Moreover, since a base material consists of a high degreeof-hardness metal of the high-melting point of cubic system, intensity is high and it can apply also to the use on which mechanical stress tends to act. [0032] moreover, superconductivity according to claim 2, if it is in a conductor Since it consists of a high degree-of-hardness metal of the high-melting point of cubic system, the base material made into rolling texture, the stacking-tendency polycrystal interlayer formed on this base material, and the oxide superconductivity layer formed on this stacking-tendency polycrystal interlayer are provided and it is characterized by the bird clapper While what has the good polycrystal interlayer of a stacking tendency easily on the good base material of the stacking tendency made into rolling texture is obtained The crystal stacking tendency of the oxide superconductivity layer formed on a stacking-tendency polycrystal interlayer can also obtain the oxide superconductivity layer which could be made to carry out orientation easily according to a stacking-tendency polycrystal interlayer, was excellent in the crystal stacking tendency as a result, and was excellent in the superconductivity property. moreover, magnetic field application uses, such as a super-conductive magnet, a superconductivity electric organ, etc. on which intensity is high and mechanical stress tends to act since a base material consists of a high degree-of-hardness metal of the high-melting point of cubic system, -also receiving -- intensity ---like -- it is applicable satisfactory [0033] Next, in invention according to claim 3, it can consider as a recrystallization texture by performing strip processing of 90% or more of workability at the temperature more than a recrystallizing temperature, and forming a base material to the material which consists of a high degree-of-hardness metal of the highmelting point of cubic system, and can consider as the good base material of a crystal stacking tendency. By and the thing for which an ion beam is irradiated from across and a stacking-tendency polycrystal interlayer is formed at the same time it makes an interlayer's constituent particle deposit on this base material In case it leaves alternatively only the good atom of the good crystal stacking tendency of a list and it is made to deposit, removing the atom which is made to deposit the atom which should constitute a stacking-tendency polycrystal thin film on a base material, and is in the bad unstable position of a list by the ion beam Since an atom can be made to deposit with the priority to the good state of the good stacking tendency of a list according to the stacking tendency of a stackingtendency base material in the initial stage of deposition, the good stackingtendency polycrystal interlayer of a stacking tendency can be formed in time shorter than before so that the stacking tendency of a base material may be met. moreover, the oxide superconductivity which was excellent in the superconductivity property which forms an oxide-superconductivity layer, and

which was excellent in the transition-current property as a result since it had by the good crystal stacking tendency on the stacking-tendency polycrystal interlayer and the oxide-superconductivity layer could be formed when becoming on the stacking-tendency polycrystal interlayer — a conductor can manufacture in time shorter than the conventional method, and there is an effect which can improve manufacture efficiency

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] the oxide superconductivity equipped with the polycrystal thin film concerning this invention — it is the cross section showing the 1st operation gestalt of a conductor

[Drawing 2] the oxide superconductivity equipped with the polycrystal thin film concerning this invention — it is the cross section showing the 2nd operation gestalt of a conductor

[Drawing 3] It is the outline block diagram showing an example of the manufacturing installation of the polycrystal thin film used in case the polycrystal thin film of this invention is manufactured.

[Drawing 4] It is the cross section showing an example of the polycrystal thin film obtained by enforcing the manufacture method of the conventional polycrystal thin film.

[Drawing 5] It is the cross section showing other examples of the polycrystal thin film obtained by enforcing the manufacture method of the conventional polycrystal thin film.

[Drawing 6] It is the conceptual diagram of the equipment for measuring the crystal stacking tendency of a polycrystal thin film.

[Drawing 7] It is the schematic drawing showing the crystal stacking tendency of the crystal grain which constitutes a polycrystal thin film.

[Description of Notations]

1 ... a base material and 2 ... a stacking-tendency polycrystal thin film (stacking-tendency polycrystal interlayer), 3, and 3' ... a polycrystal base material and 4 ... an oxide superconductivity layer (stacking-tendency stratum functionale), 5, and 5' ...

oxide superconductivity -- a conductor

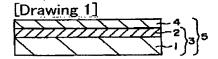
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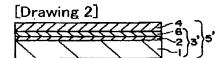
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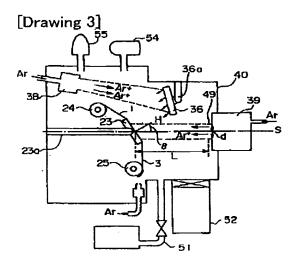
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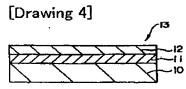
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DRAWINGS

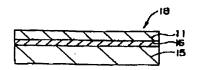


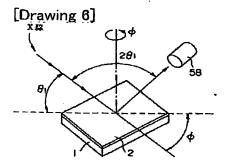




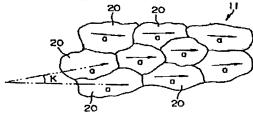


[Drawing 5]





[Drawing 7]



[Translation done.]